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# Thickness of Inhibiting Films on Glass Electrode Surfaces

By Donald Hubbard and Gerald F. Rynders

The thickness of voltage-inhibiting films produced on glass surfaces by heat treatment after leaching has been studied by means of the glass electrode and the interferometer procedure previously used for determining the chemical durability of glasses. The glass electrode gave conspicuous voltage departures (errors) and alterations (swelling) of the surface that were just detectable by the interferometer. This corresponds to approximately 0.01 fringe, or four times the unit cell dimension for cristobalite. The inhibiting effect of films of electric conductors, such as metallic silver, has been qualitatively compared with the inhibiting effect of films prepared from electric nonconductors, such as petrolatum and silicone stopcock grease.

## I. Introduction

Considerable interest in the general subject of glass surfaces has been aroused by many industrial and scientific problems involving glass solution interfaces. Examples of these problems include the commercial practice of improving the chemical durability of inferior glasses by various surface treatments, the application of nonreflecting films to the surfaces of optical elements, and the effect of nonhygroscopic films on the hydrogen-electrode function of the glass electrode.

From earlier work it is obvious that the glass electrode is an extremely sensitive indicator capable of detecting the presence of inhibiting films thinner than $6\times10^{-6}$ cm, and the interferometer can readily detect alterations of an optically flat surface of less than one-tenth this value. The voltages of glass electrodes [1, 2, 3] [1] prepared from Corning 015 [4] or other glasses of adequate hygroscopicity [5, 6, 7] and satisfactory chemical durability [7, 8] follow approximately the straight-line relation of the Nernst equation [9] over an extended range of hydrogen-ion activities [10]. Normally, the glass electrode exhibits voltage departures from the theoretical in the extreme acid [11, 12] and alkaline ranges [3, 13]. However, under special conditions of annealing or other controlled heat treatments after aging (leaching in acid solutions) the electrodes develop very large voltage departures (errors) over the entire pH range [14, 15, 16].

In extreme cases the hydrogen-electrode function (pH response) of the glass disappears almost completely, and the electrodes behave similarly to electrodes prepared from glasses of low hygroscopicity [6, 17]. This loss of pH response is brought about by the formation over the entire surface of the electrode bulb of a thin, nonhygroscopic, silica-rich layer [16]. With the interferometer method previously used for the determination of the chemical durability of glasses [7, 18, 19, 20], the maximum thickness of these inhibiting layers was estimated to be approximately $6\times10^{-6}$ cm [16].

The present investigation was undertaken to determine what further information concerning the thickness of these films might be obtained from the combined use of the glass electrode and the interferometer.

## II. Experimental Procedure

A series of mercury-filled glass electrodes [6, 21, 22] prepared from Corning 015 glass was leached in Britton-Robinson universal buffer [23] at pH 4.6 for various periods of time at 80° C. With the mercury removed, these leached electrodes were heated to 550° C, held 10 minutes and cooled slowly to 400° C, then cooled more rapidly to room temperature [16]. This series was prepared in order to ascertain the time of leaching necessary to develop an inhibiting film sufficiently thick to

[1] Figures in brackets indicate the literature references at the end of this paper.

bring about detectable voltage departures. Other glass electrodes, without previous leaching or annealing, were coated with inhibiting films of nonhygroscopic materials, such as silicone stopcock grease, petrolatum, and metallic silver.

The hydrogen-electrode function of all experimental electrodes was determined with a Beckman pH meter model *G*, using a well-conditioned glass electrode as the reference electrode. The voltage-departure measurements [16] were confined to a pH range over which the glass electrode is known to give reliable readings.

In order to determine the alterations of the electrode surface during the period of leaching, pitch-polished, optically flat specimens (approximately 2.5 by 1.5 cm) of Corning 015 glass were partially immersed in the same buffer as the electrodes and given identical treatment. The surface of the buffer was covered with a thin layer of liquid petrolatum to prevent evaporation of the solution during the period of exposure. The magnitude of the swelling of the glass surface was determined by observing the displacement of the interference fringes when the specimens were placed under an optical flat of fused silica [7, 20]. This displacement was converted to centimeters by the formula

$$\text{Swelling in centimeters} = \frac{N}{2} \times 5{,}876 \times 10^{-8},$$

where $N$ is the number of orders (fringes), and 5,876 angstroms is the wavelength of the principal helium line.

The thickness of the silver layers deposited on the electrodes was determined by the interferometer on optical flats of Corning 015 glass coated simultaneously along with the glass electrodes. A small area of silver was stripped from these silver-coated flats by the use of chromic acid, and the displacement of interference fringes was observed. No satisfactory method was developed for determining the thickness of the petrolatum anh silicone layers.

## III. Results and Discussion

### 1. Films Formed by Leaching and Annealing

The data listed in table 1 and plotted in figure 1 show the voltage departures brought about by heat treating at 550° C a series of Corning 015 glass electrodes previously leached at pH 4.6 for 0, 1, 2, 4, and 8 hours at 80° C. The most conspicuous feature of this series is the marked increase in the voltage departures that appears between the electrodes given 1- and 2-hour leach-

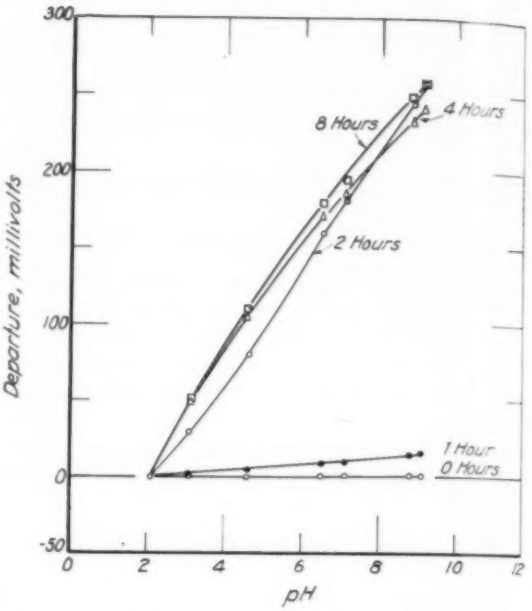


FIGURE 1. *Voltage departures of glass electrodes, leached for various periods of time in Britton-Robinson universal buffer* (pH *4.6 at 80° C) and then heated for 10 minutes at 550° C.*

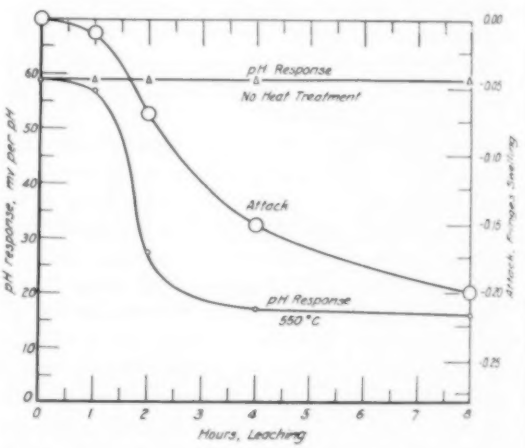


FIGURE 2. *Effect of leaching* (pH *4.6 at 80° C) and subsequent heat treatment at 550° C on the* pH *response of glass electrodes, compared with the attack (swelling) accompanying the leaching.*

ing periods. Although there is some overlapping of the voltage-departure curves for the electrodes given 2-, 4-, and 8-hour leaching, it is obvious that most of the effective inhibiting layer is formed within 2 hours. Converting the voltage departures between pH 2.1 and pH 4.6 to pH response (millivolts per pH) gives the value for the departure curve plotted for 550° C in figure 2. From this curve the loss in hydrogen-electrode function with increasing duration of leaching treatment can be compared directly with the amount of swelling of the glass (listed in table 1 and plotted as negative values in figure 2) brought about by the same period of leaching.

TABLE 1. *Voltage departure and* pH *response of electrodes in solutions of various* pH *values after leaching in a solution at* pH *4.6 for various times at 80° C and heat treating at 550° C*

[The attack (swelling) exhibited by the glass under these conditions of leaching is given]

| Leaching time | Voltage departure at pH— | | | | | | | pH response [1] | | Attack (swelling) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2.1 | 3.1 | 4.6 | 6.5 | 7.1 | 8.8 | 9.1 | No heat treatment | Heated to 550° C | Observed | Used in calculation | Plotted in figure 3 |
| *hr* | *mv* | *mv* | *mv* | *mv* | *mv* | *mv* | *mv* | *mv/pH* | *mv/pH* | *Fringes* | *Fringes* | *cm* |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 59 | 59 | 0 | 0 | 0 |
| 1 | 0 | 2 | 5 | 8 | 9 | 14 | 16 | 59 | 57 | Detectable | 0.01 | $0.3\times10^{-6}$ |
| 2 | 0 | 29 | 79 | 159 | 181 | 243 | 257 | 59 | 27.4 | <0.1 | .07 | 2.1 |
| 4 | 0 | 49 | 105 | 171 | 185 | 232 | 239 | 59 | 17 | > .1 | .15 | 4.4 |
| 8 | 0 | 51 | 108 | 179 | 195 | 248 | 257 | 59 | 15.8 | <1/4 | .2 | 5.9 |

[1] pH response calculated from voltage departures at pH 2.1 and 4.6.

Figure 3, which was also plotted from the data in table 1, gives an over-all picture of the effect of thickness of the inhibiting film on the pH response of these glass electrodes. From this curve, it is obvious that the major portion of the inhibiting effect takes place for film thicknesses between $0.29\times10^{-6}$ and $2.05\times10^{-6}$ cm.

If the edge of the unit cell of cristobalite ($7.0\times10^{-8}$ cm. [24]) is used as a reference scale, the thickness of the inhibiting layer after 1 hour of leaching is $29.0\times10^{-8}/7.0\times10^{-8}=4.1$ unit cells. That some of this swollen layer does not contribute to the effective voltage-inhibiting layer was shown in the earlier work [16] by the hygroscopicity of the annealed leached film. In that investigation the outer layer was found to be strongly water absorbent, showing that the nonhygroscopic, voltage-inhibiting film was confined to a layer formed by reaction between the base glass and the lower level of the silica-rich layer. Just what portion of this swollen surface contributes to the inhibiting layer is merely conjecture, but the evidence indicates that a layer thinner than four unit cells of cristobalite was readily detected by the glass electrode in the present investigation.

These inhibiting films were removed by immersing the electrodes for a few seconds in 1:1 hydrofluoric acid, thereby restoring the electrodes to their correct pH response [16].

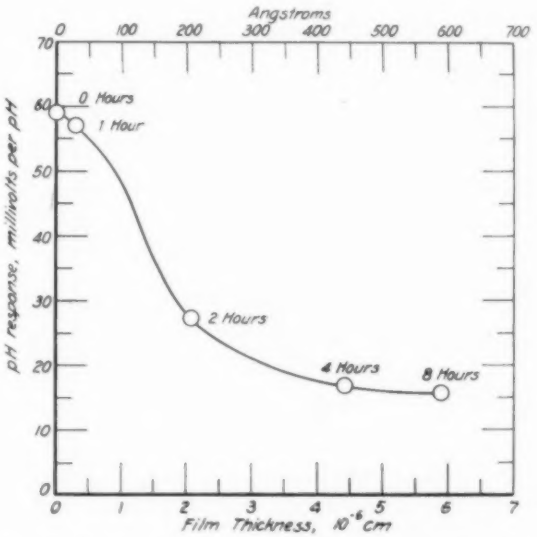


FIGURE 3. pH *response of annealed, leached glass electrodes and the accompanying limiting thickness of the inhibiting layer on the surface of the glass brought about by leaching at 80° C.*

## 2. Films of Petrolatum and Silicone

Other examples of nonhygroscopic films [25] that inhibit the pH response of the glass electrode are given in table 2 and figure 4. Curve *A* gives the voltage performance of the electrodes before the films of the electric nonconductors, silicone (stopcock grease), and petrolatum, were applied and also after these films were removed. The extent of the departures is not an indicator of the relative inhibiting capacity of the materials, as no method of film-thickness control was available. The petrolatum coatings often rendered the electrode so insensitive that no readings could be obtained with the electrometer.

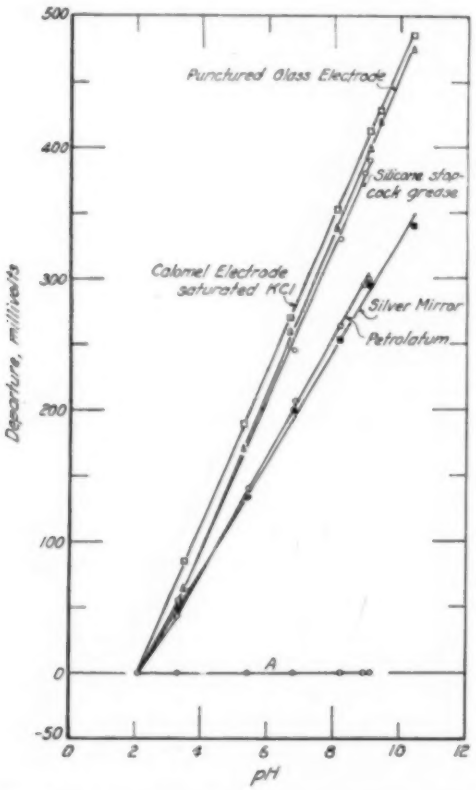


FIGURE 4. *Voltage departures of the glass electrode brought about by films of silicone stopcock grease, petrolatum, and silver compared with the voltage response of electrodes having little or no hydrogen-electrode function.*

The voltage departures brought about by a film of metallic silver are included in figure 4 to emphasize that films of electric conductors are also effective in destroying the hydrogen-electrode function of glass electrodes.

TABLE 2. *Voltage departures of glass electrodes brought about by thin films of nonhygroscopic materials, compared with the voltage performance of the saturated calomel half-cell and punctured, mercury-filled glass electrode.*

| pH | Voltage departure of glass electrodes coated with— | | | pH | Voltage performance of— | |
|---|---|---|---|---|---|---|
| | Silicone | Petrolatum | Silver | | Calomel half-cell | Punctured glass electrode |
| | *mv* | *mv* | *mv* | | *mv* | *mv* |
| 2.1 | 0 | 0 | 0 | 2.1 | 0 | 0 |
| 3.3 | 53 | 43 | 48 | 3.5 | 85 | 66 |
| 5.4 | 171 | 141 | 133 | 5.3 | 189 | 171 |
| 6.8 | 245 | 207 | 190 | 6.7 | 270 | 259 |
| 8.2 | 330 | 263 | 252 | 8.1 | 352 | 338 |
| 8.9 | 381 | 295 | ..... | 9.1 | 412 | 399 |
| 9.1 | 389 | 299 | 295 | 9.4 | 432 | 419 |
| 10.4 | ..... | ..... | 340 | 10.3 | 486 | 475 |

It is interesting to observe that the voltage departures of these electrodes with inhibiting films approach the voltage departures observed for punctured glass electrodes (mercury filled) and the saturated calomel half-cell, figure 4. The limiting departure seems to be that dictated by an electrode having no response to hydrogen ion activity.

## 3. Films of Metallic Silver

The data plotted in figure 5 from table 3 show the voltage departures brought about by metallic silver films of different thicknesses. The voltage departures for these silver-coated electrodes, especially for the thinner silver coatings, demonstrated a tendency to drift toward zero departure prior to the recorded observations, particularly in the acid buffers. This feature was attributed to the presence of pinholes in the silver coatings. Hence the severe bow shown by two of the curves in figure 5 is believed to be spurious.

The inhibiting effect of silver films of different thicknesses on the pH response of glass electrodes is shown by the data given in table 3 and plotted in figure 6. The effect of the electrically conducting silver films applied to the outer surface of these electrodes is qualitatively similar to that for the silica-rich nonhygroscopic films obtained by leaching and annealing, and is also similar to the water-repellent coatings of petrolatum and silicone stopcock grease.

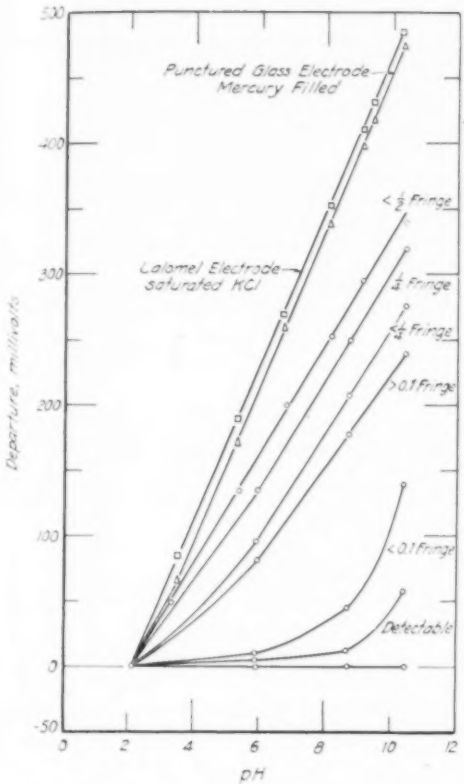


FIGURE 5. *Voltage departures of glass electrodes brought about by thin films of metallic silver compared with the voltage departure of electrodes having little or no hydrogen-electrode function.*

TABLE 3. *Voltage departures and* pH *response of glass electrodes brought about by metallic-silver films of various thicknesses*

| Film thickness observed | Voltage departure at pH— | | | | pH response [1] | Film thickness | |
|---|---|---|---|---|---|---|---|
| | 2.1 | 5.9 | 8.1 | 10.4 | | Used in calculation | Plotted values |
| *Fringes* | *mv* | *mv* | *mv* | *mv* | *mv/pH* | *Fringes* | *cm* |
| 0 | 0 | 0 | 0 | 0 | 59 | 0 | 0 |
| (3) | 0 | 6 | 12 | 57 | 52.1 | 0.01 | $0.3 \times 10^{-6}$ |
| <0.1 | 0 | 10 | 46 | 139 | 42.2 | .07 | 2.1 |
| >.1 | 0 | 81 | 177 | 239 | 30.2 | .15 | 4.4 |
| <1/4 | 0 | 96 | 207 | 276 | 25.7 | .2 | 5.9 |
| 1/4 | 0 | 134 | 249 | 319 | 20.6 | .25 | 7.3 |
| <1/2 | (3) | (3) | (3) | (3) | 18 | .45 | 13.2 |

[1] pH response calculated from voltage departures at pH 2.1 and 10.4.
[2] Detectable.
[3] See table 2, column 4.

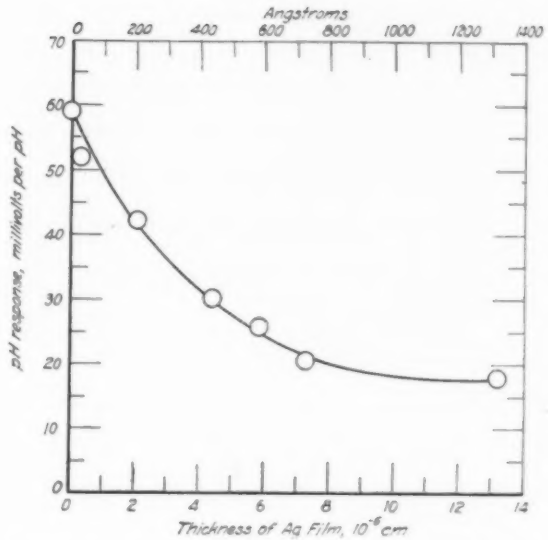


FIGURE 6. *Inhibiting effect of silver films of different thicknesses on the* pH *function of glass electrodes.*

### 4. Voltage Departure with Reference to Sodium-Ion Concentration

Voltage departures exhibited by glass electrodes have frequently been accredited to an equilibrative response to ions other than hydrogen [26] such as $Na^+$. In the present investigation, there is no theoretical reason for attributing the voltage departures of the glass electrode brought about by the inhibiting films to a response of the electrodes to $[Na^+]$ of the buffers used. However, it is obvious that a thickness for any of the inhibiting films could be selected that would present a pseudo-correct response to the $[Na^+]$.

## IV. Conclusions

The glass electrode readily detects the presence of certain voltage-inhibiting films as thin as 30 angstroms. This sensitivity approaches the practical limits of resolution of the electron microscope and the interferometer. Films of electrical conductors, such as silver, and electrical nonconductors, such as petrolatum, when applied to the outer surface, appear to be equally effective in inhibiting the pH function of the glass electrode. A study of the nature of these films may lead to a more satisfactory picture of the mechanism of the glass electrode.

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WASHINGTON, May 13, 1948.

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# Light-Sensitive Papers as Controls for Testing Textile Colorfastness and Stability of Materials Under Arc Lamp Exposure

By Herbert F. Launer

A simple method of control of the integrated exposure of the fluctuating arc lamps used in the textile and other industries for testing lightfastness of textile dyeings and stability toward light of materials in general, is described. A piece of light-sensitive paper is placed in lamps along with materials to be tested, and the exposure is terminated when a match with a standard, observable with the unaided eye, is obtained. The standard is a strip of the same batch of paper that has been exposed in a master lamp to a definite light dosage. The method is based upon standard light quantities and is thus largely independent of variation between batches of light-sensitive paper.

The variations among fading lamps used in the textile industry and the causes, such as differences in lamp models, and line voltage, are discussed. A 4-percent difference in line voltage leads to a difference in radiant output of 11 percent in the waveband from 300 to 480 millimicrons, the region probably causing most of the fading of dyed textiles. Variations in line voltage considerably larger than 4 percent are probable in many communities.

The papers were made in batches of 20 to 30 thousand test pieces by dip-dyeing special cotton-rag or wood-fibers papers with aqueous solutions of Niagara Blue G, or with Victoria Blue B in aqueous ethanol. One paper was made by beater-dyeing wood fibers with Niagara Blue G to give a nonleaching paper and was sized with melamine resin to impart high wet strength, making the paper suitable for lamps with water spray. Other paper-dye combinations were studied.

Data are presented indicating the visual sensitivity of the various types of papers from 1 to 100 hours of usual arc exposure, the permanence of the papers during storage in the dark, the uniformity throughout each batch, and the effect of nonuniformity, temperature effect, lasting qualities of the standard strips during use, correlation with textile dyeings, and the effect of intermittent exposure.

The master lamp used for standardizing the papers, its accessories, and reproducibility of input power and radiant output are discussed.

## I. Introduction

The textile and other industries use carbon arcs r the testing of colorfastness of dyed fabrics and stability of materials in general to light. There considerable variation in performance among mps and of a given lamp from time to time. nce the testing is predicated upon comparable rformance of such lamps, variation introduces certainties and frequently vitiates the results.

The extent of such variation has been the subject of recent surveys by Wood [1],[1] the National Bureau of Standards [2], and Seibert [3]. The results of all three, obtained by distributing various types of dyed materials for test in large numbers of lamps, showed the variations to be very large. Seibert, in particular, showed that some of the weakest lamps required from two to

[1] Figures in brackets indicate the literature references at the end of this paper.

three times as long to produce the same fading as the strongest lamps, and that over one-third of the lamps deviated by more than 15 percent from average.

Although practically all textile fading lamps are of one manufacture (Fade-Ometer) and involve the same fundamental arc characteristics, they differ among the several models as to type of current (alternating or direct), as to power input, and in the arrangements for thermostating, humidifying, and exposing the samples. Such differences in design probably give rise to differences in performance among the various installations [4].

The differences, however, in fading action among identical models, or in a given lamp appear to arise from variations in line voltage. The radiant output in the spectral region, approximately 300 to 480 $m\mu$, probably the most generally effective spectral region in such lamps, changes by 11 percent for a 4-percent change in line voltage.[2]

Data were obtained by regulating, at various values, the line voltage of an alternating-current F D A–R model Atlas Fade-Ometer and measuring the corresponding relative radiant output with an RCA 929 phototube—Corning 5850 filter combination, having a spectral maximum near 385 $m\mu$., in a circuit with General Electric recording microammeter. Typical data were as follows, integrated over ½-hr periods:

| Line voltage | Relative phototube response |
|---|---|
| | *μ amp* |
| 217 | 6. 0 |
| 228 | 6. 8 |
| 238 | 7. 7 |

Voltage variations at most substations in the District of Columbia are about 4 percent,[3] which is probably exceeded in most communities. To this must be added the variable voltage drop in the mains, transformers, and individual plant wiring, which may be as high as 11 percent [6].

Another factor is the gradual decrease in ultraviolet near the transmission cut-off of the glass enclosures, through solarization of the glass. However, Cady and Appel [7], who exposed 1,252 textile dyeings to sunlight, showed little difference in fading with and without intervening window glass. Cady and Smith [8] found little difference in the fading of 40 dyeings exposed to the Fade-Ometer with plain and with Corex-D glass globes, which indicates that that region of transmission of glass most affected by solarization, namely, below 330 $m\mu$, may not be of decisive importance for textiles. The visible discoloration of the glass caused by extended use may cause considerable difference between lamps.

Since uniform performance of arc lamps is a practical impossibility at present, recourse must be had to a method of exposure control by estimating radiant output with a light-sensitive material.

Simple methods of exposure control have been described before. Krais [9] used the light-sensitive dye Victoria Blue R on china clay, the latter then brushed on to paper, Robson [10] used eosin on a filter paper, Scott [11] used Victoria Blue B on silk, and Clark [12] used zinc sulfide on paper.

A method using a light-sensitive solution is that proposed by Werkenthin [13] and his associates of the Bureau of Ships, U. S. Navy, for the control of arc performance in the testing of rubber, in which a solution containing essentially uranyl oxalate in a silica cell is exposed to the arc. The method is a noteworthy, successful attempt to systematize the use of testing arcs, but it is not simple to use, and in its present form is limited to exposures of approximately ½-hr duration. Other details of the method have been studied by Greider and Bowditch [14].

A control for fading lamps has been discussed by Wood [1], who studied various combinations of dyes and appropriate vehicles, such as silk, wool and cotton textiles, paper, etc., and found Formyl Violet S4B on nylon to be the most sensitive. An arc was used as a master, or reference, lamp, but the idea was discarded when it was found that the lamp changed 20 percent in 4 months.

Christison [15] recognized the desirability of a master lamp, but in its absence stressed the reproducibility of shade (rather than of fading rate) of the blended wool materials he developed, which have since been adopted by the AATCC for the grading of dyeings into classes of lightfastness

[2] An unpublished paper presented at a symposium on light aging at The Bureau of Ships, Navy Department, Washington, D. C., Oct. 1945, at a meeting of the Technical Association of the Pulp & Paper Industry, New York City, Feb. 1946, and at a meeting of the American Association of Textile Chemists & Colorists, Philadelphia, Pa., April 1945 [2, 5].

[3] Quoted with the permission of George Bisset, Potomac Electric Power Co.

differing by steps of 100 percent. However, these materials, of which Cady [16] has given historical background, were intended for only rough control.

Seibert [3] proposed a procedure employing a light-sensitive gray paper and gray cotton, with standards based upon a fixed "percentage color change," determined from reflectance measurements. His materials were distributed to a number of lamp users and showed the difference in exposure periods among the various lamps that were necessary to reach a given extent of fading. The materials, however, were rather insensitive to time differences under 20 percent.

In the above methods, the standard with which the light-sensitive materials are compared, in estimating exposure, is either "colorlessness," [9, 10], which is difficult to evaluate, or some final shade [11, 12, 3], defined by preserving a sample or by means of a spectrophotometric reflectance curve. With such a standard, the light-sensitive materials must be reproducible in fading rate from batch to batch, as otherwise the amount of exposure necessary to match the standard may vary for each batch, thus nullifying the method to that extent.

The present article describes a method based upon standards produced with reproducible light dosages, rather than from reproducible batches of the light-sensitive media. The method has been found to be generally satisfactory in large-scale application to textile fading and lamp calibration, [2, 5].

The freedom from the difficulties of batch reproducibility, the ease of recognizing extent of exposure, the reasonable assurance of uniformity within each batch, the wise range of exposure periods available, and the general standardization of procedure constitute the main advantages of the method.

## II. Principles of Method of Control of Lamp Performance With Light-Sensitive Papers

Special paper was made and dyed with a light-sensitive dye in quantities of 20 to 30 thousand test pieces per batch in the experimental paper mill at the Bureau.

A portion of the batch is standardized in a master lamp by exposing it to a convenient, measured light dosage, defined in terms of "standard arc hours." This standardized paper becomes the secondary standard used to gage light dosage in other lamps.

In a typical application, a piece of light-sensitive paper is simultaneously exposed with materials being tested in a lamp. When a match between the test piece and the secondary standard is observed with the unaided eye, the materials are assumed to have received the corresponding light dosage. Estimating the degree of under- or over-exposure is facilitated by auxiliary standard strips representing 80, 90, 110, and 120 percent of the light dosage.

The actual time of exposure is thus immaterial, unless it differs consistently, perhaps 30 percent or more, from the number of standard arc hours identified with the exposure, indicating that an adjustment on the lamp may be desirable.

This method has as its fundamental basis the production of secondary standards from each batch of light-sensitive paper, with a definite, reproducible dosage of light. Thus the batches can, and do, vary, or the paper type may be changed without affecting the validity of the method.

Light-sensitive papers can be used, without secondary standards, as light-totaling devices in photochemical or other research with a given source of light. Relative intensities in many parts, otherwise inaccessible, of a given system may be simultaneously measured very simply. The papers dyed with Niagara blue were found to be colorimetrically unaffected by ozone and may thus be used near quartz mercury lamps or lamps of the germicidal type. Combined with photometric measurement of reflectance, precision in using light-sensitive papers may be expected to equal that of acceptable radiometric technique.

## III. Light-Sensitive Papers

A variety of types of light-sensitive papers were developed for various periods of exposure and for exposure in lamps with water spray. The method requires that the papers be colorimetrically stable in the dark, both unexposed and exposed samples, producible in large uniform batches, normally responsive to temperature, arc characteristics, and relative humidity, and visually sensitive, as defined by the additional exposure, expressed in percentage

of the light dosage already received, necessary to produce a change observable with the unaided eye.

### 1. Components and Methods of Dyeing

Fifteen kinds of experimental papers, varying in type of cellulose, filler, sizing, and finish were dyed and irradiated to determine the optimum characteristics of papers for the work. Two neutral (pH 6.8) unsized papers were then produced in the Bureau's paper mill. Paper 1444 was made entirely from wood pulps (80% No. 1 soft alpha, 20% hardwood sulfite pulps), and paper 1370 was entirely of cotton origin (40% new rags, 40% old rags, 20% clay). Papers of these types show considerable cellulose stability.

These two papers were tested with 47 representative dyes at various concentrations. It was found that National Aniline Niagara Blue G Conc., lot 64704, Colour Index 502, and, to a lesser extent, DuPont Victoria Blue B, Conc., lot 22, Colour Index 729, gave the most useful products.

By varying dye, fiber, and method of application, papers of differing fading rates were obtained. The exposure times represent approximately the time necessary for most Atlas Fade-Ometers to fade the papers to the region of most perceptible change, which occurs when the paper has sufficient dye left for easiest judgment of the effect of further increments of light.

(a) Paper C, exposure time 3 to possibly 10 hr; paper 1370, tub-dyed with 0.09 percent of Victoria Blue in 1:3, 95-percent ethanol-tap water solution.

(b) Paper E, exposure time 10 to 40 hr. Paper 1370, tub-dyed with 0.54 percent of Niagara Blue in tap water.

(c) Paper F (or A), exposure time 40 to 100 hr. Paper 1444, tub-dyed with 0.65 percent of Niagara Blue in tap water. A somewhat lighter modification of paper F has been referred to as paper A.

(d) Paper S, exposure time 20 to 40 hr in lamps with water spray. This paper was beater-dyed by adding a solution of Niagara Blue to give a 0.5 percent ratio, dye: fibers, using the same kind of fibers as in paper 1444. Melamine resin, 3 percent of fiber weight, was added to the beater to give high wet strength for use in lamps with water spray.

These four types serve to indicate the methods of producing papers of various desired characteristics. The tub-dyed papers, which are finished papers run through a dye bath, must be used dry; the beater-dyed paper is nonleaching and may be used for "weathering" lamps, but is decidedly inferior to the tub-dyed papers in sensitivity. The tub-dyed papers have the disadvantage of tending to exhaust the dye bath, which thus requires replenishing from time to time.

### 2. Visual Sensitivity

Cooperating commercial and governmental organizations found that paper A had a visual sensitivity of 10 percent; that is, the color differences between pieces exposed for 18, 20, and 22 hr could be easily distinguished, although some observers encountered hue difficulty in matching the standardized strips with their own exposures. Investigation showed that the difficulty was eliminated if the samples were matched in the absence of the unexposed blue border of the test pieces.

Subsequently it was found that this type of dyed wood fiber paper is considerably more sensitive after 40 hrs of exposure, whereas paper E, made of cotton fibers, absorbing less of the same dye, is more sensitive at the 20-hr period.

A comparison of the visual sensitivity of the various papers is given in table 1. The results are based upon the estimates of a limited number of individuals and are probably more reliable on a relative than absolute basis.

Paper E, made from an unusually uniform, soft, base sheet had the highest sensitivity, because its smoothness of texture detracted least from shade differences. The coarser texture of the other

TABLE 1. *Minimum increments in light dosage producing visible [a] differences in light-sensitive papers*

| Types of papers | Percentage of total light dosage [b] after the following hours of exposure— | | | | |
|---|---|---|---|---|---|
| | 3 | 10 | 20 | 40 | 100 |
| C | 5 | 10 | White | White | White |
| E | 15 | 10 | 2½ | 5 | 10 |
| F (or A) | 30 | 20 | 10 | 5 | 5 |
| S (air-dry) | 30 | 20 | 15 | 15 | 15 |
| S (with spray) | 30 | 20 | 10 | 10 | White |

[a] By visible is meant a difference that can be seen, with the unaided eye, between two pieces of paper, one closely superposed upon the other, rather than differences on one piece.

[b] For example, if it is possible to distinguish between a piece exposed for 20 hr and one exposed for 20½ hr, in the usual Atlas Fade-Ometer, the increment producing a visible difference is expressed as 2½ percent.

papers, or the mottled appearance of faded papers using unsuitable dyes, acts like camouflage in appearing to break up the edge of two fields being compared, whereas ease of comparison depends considerably upon sharpness of borderline.

These papers were all uncalendered after dyeing, because it was found that the gain in fineness of texture was more than offset by the production of highlights due to specular reflection.

Paper S, beater-dyed, the simplest to produce, was also the most insensitive. Since all constituents were the same as in F, and since differences in the amounts of dye were largely without effect on sensitivity, the method of applying the dye must account for the difference. A beater-dyed paper can be expected to be more uniformly dyed throughout its thickness than a tub-dyed sheet, in that the latter is darker on the outside. This was strikingly so in paper C, of which the internal fibers remained white. It is, therefore, possible that a lighter interior causes greater contrast, and uniform beater-dyeing, less contrast.

The rate of fading of paper S is dependent upon the wet-dry cycle. As the ratio, time wet/total time, is increased from 0 to 30 percent, the rate increases considerably, apparently because of an accelerating effect of water, remains roughly constant to 70 percent, beyond which, to 100 percent, the rate decreases.

The decrease in rate is probably due to the lower temperatures of the paper when wet, and all of the papers sprayed over 50 percent of the time, except those continuously sprayed, showed less fading at the bottom, where the water tended to remain longer. This was not a leaching process, since papers sprayed in the dark, or those kept continuously wet during exposure, showed no inhomogeneity. The effect of temperature will be discussed in a later section. If this type of paper is used in "weathering" lamps, the wet-dry cycle should be specified. If it is used for outdoor exposures, the amount of rainfall, and, of course, temperature will be a factor.

Fading in this and other experiments was taken from reflectance measurements made at 45° from normal incidence at 578 mμ, with equipment previously described [17]. The papers were sucked flat against a black backing during measurement.

### 3. Colorimetric Stability in the Dark

During storage periods of 8 to 18 months, the papers were found not to have changed significantly, with the exception of paper C. This was found by measuring the reflectance, at various times, of 100 pieces, taken at random from each batch, the total change being within the limit of reproducibility, 0.002 reflectance, of the instrument.

Paper C, during 8 months, was found to have lost color corresponding to approximately 5 percent of its 3-hr period. This paper for short periods, therefore, must be considered unstable, but can find practical application by frequent standardization. For periods beyond 5 hr, it is probably sufficiently stable.

The other papers, both exposed and unexposed, were subjected to a rather severe process of "accelerated aging," by being kept at 100° C in the dark for 3 weeks. At the end of the time they were found to have lost color corresponding to 5 percent of a 20-hr exposure period.

### 4. Standardized Strips During Use

The standardized strips are mounted in a comparison booklet that has flexible black cellulose acetate covers to protect the strips from soiling and light during nonuse.

During use, the strips are exposed to interior daylight and artificial light. It was of interest to determine the additional fading of the strips during normal use. Some exposed pieces of paper A were placed under Corex D glass to keep out dust and exposed to the daylight of a well-lighted room for 3 weeks in the late fall of the year. This corresponded roughly to a daily exposure of 10 min for 2 yr. The reflectance change was found to be 0.004, corresponding to less than 1 hr of lamp exposure out of 20, and constituting an error of less than 5 percent for this rather severe test.

Under conditions of extreme atmospheric dryness, such as prevail in northern latitudes in winter, or in desert regions, it has been found desirable to humidify briefly, with the breath, the test piece before comparing, inasmuch as the reflectance of the warm, dry piece, just removed from a lamp operating under the extreme conditions mentioned, is too high by approximately 5-percent exposure time. Under all other conditions, including extreme humidification, the reflectance is unaffected.

During the comparison, it has been found advisable to keep the test piece in the exposure frame so that the unexposed blue border shall not have a disturbing chromatic effect.

### 5. Uniformity of Batch

The reflectances of 100 pieces each of papers C, E, F, and S, and 255 pieces of A, chosen at random, were measured. The resulting frequency distributions were analyzed statistically for standard deviation,

$$S=\sqrt{(Sfx^2-S^2fx/n)n-1},$$

which were found to be 1.07, 1.12, 1.40, 1.60, and 1.85 for papers S, E, F, A, and C, respectively, indicating increasing dispersion and nonuniformity in that order. As might be expected, the beater-dyed S was the most uniform, with the soft E a close second. Dyeing from a partially nonaqueous solution, as in the case of C, resulted in least uniformity of product.

The real test of uniformity is, of course, the uniformity of fading rate of pieces having various values of initial reflectance. Pieces within the lowest, middle, and highest reflectance ranges of each type of paper were simultaneously exposed to light dosages appropriate for each type. The changes in reflectance were then measured. It was found, for paper E, that the final reflectance was practically independent of the initial reflectance. For paper F, however, it was found that the lowest reflectance group faded 6 percent more slowly, and the highest group 5 percent more rapidly than the middle group. For papers A and C, the corresponding values were 7 and 2 percent, respectively, for both extremes. These represent the errors involved in using off-color pieces of the papers. Apparently, the papers made from cotton fibers were considerably more uniform in fading rate than those made from wood fibers.

### 6. Effect of Temperature on Fading Rate

Although the papers are stable in the dark and temperature alone has practically no effect, it was found that temperature has considerable influence during exposure to light.

The results in table 2 show that the extent of fading of two typical papers for a given exposure was considerably increased by raising the temperature. The effect is seen to decrease with rising temperature, and as the AATCC specification for air temperature in the Fade-Ometer is 46° C, the temperatures of various materials therein will be near the higher values.

From the results in table 2 for papers E and A, neglecting the last value for the latter and using instead a value obtained from a smooth curve, and from the fading rates of the two papers, it can be estimated that an error of 10 percent would occur using the paper in two lamps operating at 40° and 50° C, disregarding the fact that the materials being tested may also show temperature effects and thereby decrease the error. It is obvious that temperature specifications for the testing of all materials are necessary if the paper is to perform satisfactorily.

TABLE 2. *Fading rate of papers A and E as a function of temperature*

| Temperature [a] of paper | Change in reflectance | |
|---|---|---|
| | Paper A | Paper E |
| °C | | |
| 20 | 0.083 | 0.179 |
| 30 | .109 | .225 |
| 40 | .130 | .262 |
| 50 | .142 | .302 |
| 60 | .143 | .329 |

[a] Temperatures of the papers were closely controlled during exposure by sucking the sheet against a thermostated metal backing. The light of a Fade-Ometer are, operated from controlled voltage, was passed through a 11-mm layer of cool flowing distilled water in a Corex-D cell. The relative humidity was maintained near 58% for all experiments with a solution of $NaBr$, saturated at the same temperatures as in this table. This equipment is described in detail in reference [18].

From a fundamental standpoint, the fact that the fading rates of these papers have temperature coefficients larger than unity shows that thermal reactions, with appreciable heats of activation, accompany the photochemical reaction. The temperature coefficient, corresponding to the error of 10 percent is 1.1, in fair agreement with the findings of Schwezow [19], who found coefficients ranging from 1.040 to 1.084 for four dyes in collodion films. Luckiesh and Taylor [20] found little effect of temperature on the fading of silk ribbon between 29° and 49° C, but "appreciably" more at 66° C. Both of these studies were, however, too limited in scope to allow conclusions regarding temperature coefficients of fading of textile dyeings

in general. It seems probable that temperature would affect the rate of change of textile dyeings and other materials during irradiation.

### 7. Correlation With Textile Dyeings

The trend in the design of textile fading lamps has been in the direction of closer control of temperature and relative humidity of the air in the sample space. Also, greater uniformity of spectral distribution may be expected with the increasing prevalence of installations by using alternating current, of which the voltage is more easily controllable than with direct current. Thus, with the later models it is possible to draw up standard procedures to minimize these sources of difference. However, many old models are not only in use, but validity of comparison of performance is frequently expected.

It was, therefore, desirable to determine how well a light-sensitive paper could serve as a control in lamps differing in type of arc, relative humidity, and temperature in their fading action on textile dyeings.

The open-arc lamp, in which the humidity could be varied over a wide range, since the humidifier consisted of an electrically heated water trough, was used for this experiment. Two sets of conditions, probably more extreme than general practice, were used: dry trough, relative humidity 13 percent, air temperature 38° C; water in the trough at 85° C, relative humidity 37 percent, with air temperature 54° C. Textile dyeings were exposed under both sets of conditions to the same reflectance of paper A, and the reflectances of the dyeings were measured, before and after exposure at 436, 546, and 578 $\mu$. The results at the wavelength of greatest reflectance change, which for all of the dyeings studied was one of the latter two wavelengths, usually agreed well with visual judgment.

The results showed that the fading rates of paper A and of most textile dyeings studied were affected to much the same extent by moisture and temperature. Of 42 dyeings, 22 faded equally (within 5 % of reflectance change), 17 faded less and 3 faded more, at the higher temperature and relative humidity.

In another series of experiments, dyeings were exposed in two widely differing lamps, enclosed and open arc, to the same reflectance of paper A. Of 33 dyeings, 16 faded equally, 13 faded more under the enclosed arc, and 4 faded more under the open arc.

In spite of the agreement, however, the results, even for the limited numbers of dyeings, indicate the desirability of standardizing such factors as relative humidity, type of arc, voltage, etc., as well as temperature, in test procedures. If that were done, the method could be expected to have general validity for many types of materials.

### 8. Effect of Interrupting Exposure

The light-sensitive papers showed excessive fading whenever the exposure was interrupted through failure of the arc in overnight runs. Paper E, for example, changed in reflectance by 0.158 for a continuous 16-hr exposure, whereas for two 8-hr exposures, interrupted by 16 hr. of darkness (during which no changes occurred), the reflectance change was 0.200. Further, if instead of 20 hr continuous exposure, interruptions of 1, 2, 3, or 4 hr occurred at 16 hr, followed by 4 additional hr of exposure, the increase in reflectance change over continuous exposure was 0.013, average, after all four periods of interruption. (In all of these experiments the arc was allowed to reach normal operating conditions before exposure.)

This intermittancy effect in light-sensitive papers, and perhaps also in textile dyeings and other materials, requires a more extended study, which is beyond the present scope.

## IV. Master Lamp for Standardizing Light-Sensitive Papers

The original intent was to develop a lamp that would provide a given light dosage, and fractions thereof, in given time periods, the light dosage being related to a given number of photons of constant wavelength distribution. The various measures to be described resulted in a lamp in which a given light dosage could be reproduced, but it was not possible to obtain a precise fraction of such a dosage, that is, 80, 90, etc., percent, for the auxiliary standard strips, because of variation of electrode resistance during the burning of the carbon electrodes. For this reason light dosage is measured by means of a "exposure meter." This is an adaptation, to high intensity sources, of a device developed by Douglas [21] for the

measurement, over periods of time, of extremely small quantities of light. This device will be described in detail in a subsequent publication.

### 1. Lamp and Accessories

During operation, the globe of the enclosed arc acquires a deposit of soot and ash from the electrodes, varying in thickness and transmittance, apparently as a function of the composition of the arc gases and of the ash content of the electrodes and thus changes the radiant output. Therefore, an arc was used that burns in a current of air that removes the arc residues and makes deposition negligible upon the 18-cm Corex-D tube that surrounds the arc and aids materially in simulating the fading action of the enclosed arc by providing a short-wave cutoff near 290 mμ.

The open arc burns cored electrodes, and as the nature of the core material determines to a great extent the spectral distribution of the arc, it is necessary that the electrodes be uniform throughout the batch. An effort was made to achieve this by purchasing a large quantity of electrodes, specially manufactured at one time from one lot of ingredients, culled to very close tolerances as to diameter.

During standardization the paper is mounted on a drum rotating at 1 rpm around the arc. The vertical face of the drum was machined to within 0.003 in. of perfectly circular and the paper mounted under tension against the machined face by wrapping around the drum, thus minimizing any tendency toward curvature in the other direction. As the paper extends downward from the drum by 5 cm, and its midpoint is 25 cm from the arc (which, furthermore, is not a point source but is about 15 mm long), the amounts of incident radiant energy differ vertically over the paper by less than 1 percent, and probably not at all horizontally, during rotation.

The lamp is housed in a special room at 25 ±0.5° C and 50 ±1 percent relative humidity, in order to avoid seasonal effects.

### 2. Power Input to Arc

Regulation of arc current and line voltage is necessary for reproducible performance of the arc.

A device, which is essentially a contact-making ammeter, regulates the arc current at 30 amp by controlling a reversible motor that regulates the arc gap.

The line voltage is kept within a tolerance of ±0.5 percent by means of an induction voltage regulator, mechanical type.

The line voltage is applied to a fixed transformer that operates the arc near 40 v.

Constant power input during the burning of a trim of the carbon electrodes is not obtained by regulating line voltage, because the IR-drop in the electrodes changes with length. In a typical case, as the electrodes were consumed, the carbon resistance [4] changed from 0.19 to 0.44 ohm, and the electrode holder voltage (the "arc" volts actually measured) changed from 42.5 to 40.5, the current remaining at 30 amps. From these values it can be calculated that the true arc voltage rose from 36.7 to 39.2, accompanied by a rise in power input.

### 3. Reproducibility of the Arc

By limiting the tests to a definite portion of the electrodes, it was possible to obtain a measure of the reproducibility of the arc by relating radiant output to power input.

The experiments were spread over a period of 2 weeks, each test as described in the footnotes of table 3. An exposure meter, the receiver of which was mounted on a drum rotating at 1 rpm around the arc, thus scanning it from all angles, was used to measure radiant output.

The results in table 3 show the following: (1) The power input to the arc is quite reproducible, as the coefficient of variation in the wattage was only 0.59 percent, with an extreme difference of 2.7 percent. (2) The radiant output, in terms of counts per hour and counts per watthour, is reproducible to the extent indicated by the corresponding coefficient of variation, and the extreme differences. This reproducibility reflects variations among electrodes, variations in average line voltage, shifts in wavelength distribution, as the exposure meter is spectrally selective, and errors in the latter. Since, in ordinary practice, triple trims of electrodes are burned simultaneously, electrode variations will probably be less than indicated.

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The problem of variations among textile fading lamps was suggested by William D. Appel. Members of the lightfastness committees of the

[4] Data furnished through the cooperation of F. T. Bowditch of the National Carbon Co., Cleveland, Ohio.

TABLE 3. *Reproducibility of master lamp in the spectral region [a] approximately 300 to 480 m, mμ*

| Run [b] | Time | Arc power [c] | "Photon counter" values | |
|---|---|---|---|---|
| | | | Counts per hour | Counts per watt-hour |
| | *min* | *w* | | |
| 1 | 113.0 | 1,062 | 1,311 | 1.234 |
| 2 | 112.0 | 1,071 | 1,322 | 1.234 |
| 3 | 111.9 | 1,072 | 1,297 | 1.210 |
| 4 | 111.8 | 1,073 | 1,300 | 1.212 |
| 5 | 111.2 | 1,079 | 1,292 | 1.198 |
| 6 | 111.6 | 1,075 | 1,289 | 1.199 |
| 7 | 111.5 | 1,076 | 1,293 | 1.202 |
| 8 | 112.3 | 1,068 | 1,293 | 1.210 |
| 9 | 111.4 | 1,077 | 1,280 | 1.188 |
| 10 | 111.8 | 1,073 | 1,276 | 1.188 |
| 11 | 111.9 | 1,072 | 1,299 | 1.212 |
| 12 | 111.0 | 1,081 | 1,293 | 1.196 |
| 13 | 111.2 | 1,079 | 1,294 | 1.200 |
| 14 | 111.6 | 1,075 | 1,312 | 1.220 |
| 15 | 110.5 | 1,086 | 1,312 | 1.208 |
| 16 | 110.0 | 1,091 | 1,303 | 1.194 |
| 17 | 111.4 | 1,077 | 1,293 | 1.200 |
| 18 | 111.8 | 1,073 | 1,306 | 1.217 |
| 19 | 111.4 | 1,077 | 1,290 | 1.198 |
| Mean | | 1,076 | 1,298 | 1.206 |
| Standard deviation [d] | | 6.31 | 11.4 | 0.013 |
| Coefficient of variation, [e] percent | | 0.59 | 0.88 | 1.1 |
| Extreme difference, percent | | 2.7 | 3.5 | 3.8 |

[a] The spectral region was defined by the spectral sensitivity and transmission curves of the RCA 929 high-vacuum phototube and the Corning 5850 polished filter, respectively, the maximum occurring near 385 $m\mu$ (manufacturers' data).

[b] A fresh single trim of cored carbon electrodes was used for each run, and the measurements were started 60 minutes after the first striking of the arc.

[c] The energy input to the arc for each run was 2000.0 watthours, measured with a Rotating Standard watthour meter, General Electric model IB9Y, capable of being read to 0.01 watthour, using the proper current and voltage transformers. Thus, the number of counts were divided by 2,000 to obtain the values of counts per watthour. The values for watts were obtained by dividing watthours by hours.

[d] Standard Deviation $= \sqrt{\frac{(x_1-\bar{x})^2+\ \ldots\ +(x_n-\bar{x})^2}{n-1}}$

[e] Coefficient of variation = 100S/mean.

American Association of Textile Chemists & Colorists and the American Society for Testing Materials cooperated. Merle B. Shaw, Martin J. O'Leary and Joshua K. Missimer, under the general supervision of B. W. Scribner, Chief of the Paper Section, rendered the indispensible aid of making and dyeing all the papers. Paul J. Shouse made some of the measurements and equipment.

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# Expansive Characteristics of Hydrated Limes and the Development of an Autoclave Test for Soundness

By Lansing S. Wells, Walter F. Clarke, and Ernest M. Levin

A technique for preparing, curing, and autoclaving 1- by 1- by 10-inch cement-lime bars was developed, and the expansive characteristics of 80 commercial hydrated limes were determined. On the basis of chemical analysis and percentage of unhydrated oxide, the hydrated limes were classified into four series: high-calcium, regularly hydrated dolomitic, highly hydrated dolomitic, and magnesian. Data on the expansions of cement-lime bars prepared in the proportions of 2 parts cement to 1 part lime, 1 part cement to 1 part lime, and 1 part cement to 2 parts lime, by weight, and autoclaved to 295 pounds per square inch gage pressure for 3 hours, showed that bars prepared with the regularly hydrated dolomitic limes, which had the highest percentages of unhydrated oxides, had the highest percentages of expansion. The high-calcium limes, characterized, in general, by the lowest percentages of unhydrated oxides, gave the lowest percentages of expansion. Most of the highly hydrated dolomitic limes had percentages of unhydrated oxide and expansion that were comparable to those of the high-calcium limes. An increase in the proportion of lime in the cement-lime bars was attended by an increase in expansion. The method for determining the linear expansion of cement-lime bars autoclaved at a steam-gage pressure of 295 lb/in.$^2$ (equivalent to a temperature of 216° C.) was found to be reproducible, by three independent operators. The effect of 17 different portland cements on the expansion of cement-lime bars showed that the expansion values for a particular lime tended to increase as the expansion value of the constituent cement increased. Arbitrarily subtracting the expansion of the neat cement from the total expansion gave the most uniform result for the "net" expansion of the lime. With an autoclave specially modified for ascertaining the behavior of cement-lime bars during the course of autoclaving, it was found that only a slight amount of the total expansion occurred before a temperature of 150° C. was reached, but above 150° C. a rapid expansion rate was noted, which in turn tapered off before a temperature of 216° C. was reached. Retarding the rate of heating resulted in a decrease in the total expansion. Finally, from criteria set forth for a procedure for determining the soundness of hydrated limes, a test is proposed with a suggested limit of expansion of 1.0 percent.

## I. Introduction

It is highly important that a mortar or plaster, after being gaged with water and setting in place, shall not undergo appreciable change in volume. Since it was known that the hydration of the constituents of lime is attended by a marked increase in volume, a study was made at the National Bureau of Standards of the hydration of magnesia in dolomitic hydrated limes and properties [1].[1] The publication of the paper soon led to consideration of the effect (if any) of unhydrated magnesia in partially hydrated dolomitic limes, and the Bureau became interested in this problem as it relates to plaster.

Extensive surveys showed that plaster failures characterized by the formation of bulges (large blisters) in the white coat, as illustrated in

[1] Figures in brackets indicate the literature references at the end of this paper.

figures 1 and 2, were widespread. Some of the salient features of the Bureau's findings were summarized recently [2] as follows:

"(1) Not a single instance has been found where bulging occurred in a white-coat plaster made with high-calcium lime; (2) ordinary dolomitic hydrated limes contain large amounts of unhydrated MgO and little or no free CaO; (3) hydration of the free MgO to $Mg(OH)_2$ is accompanied by marked expansion; and (4) after several years, the forces set up by this hydration and attendant expansion can and do cause the formation of bulges and the shearing of the white coat from the underlying coats." A more detailed paper is being prepared on this subject.

As a result of these studies, the Bureau was requested by other Government agencies to assist in formulating a specification that would exclude partially hydrated limes containing a high percentage of unhydrated oxides. Accordingly, the following tentative amendment to Federal Specification SS–L–351 for hydrated lime [3] was prepared: "The total free (unhydrated) calcium oxide (CaO) and magnesium oxide (MgO) in the hydrated product shall not exceed 8 percent by weight (calculated on the 'as received' basis)." A method was given for determining the quantity of unhydrated oxides.

Shortly thereafter certain of the manufacturers of regularly hydrated dolomitic lime started producing a more completely hydrated lime. In most instances this has been accomplished by installing autoclaves to hydrate the lime at elevated temperatures and pressures.

The 8-percent limit of the unhydrated oxide in hydrated limes recently has been included in specifications of the American Society for Testing Materials [4], as well as in those of the American Standards Association [5] for the hydrated lime to be used in white-coat plaster.

Nevertheless, a limitation on the percentage of unhydrated oxide has been criticized on the score that the quantity of unhydrated oxide itself may not be a complete indication of the inherent expansive characteristics of a hydrated lime. Such an objection would be obviated by a performance test. Since unsoundness usually does not exhibit itself for several years, a feasible performance test must also be an accelerated one.

Consequently, the purpose of the present investigation was to study more completely the expansive characteristics of hydrated limes and to obtain data and information that might be used in formulating an accelerated performance test acceptable for a specification for the soundness of hydrated lime.

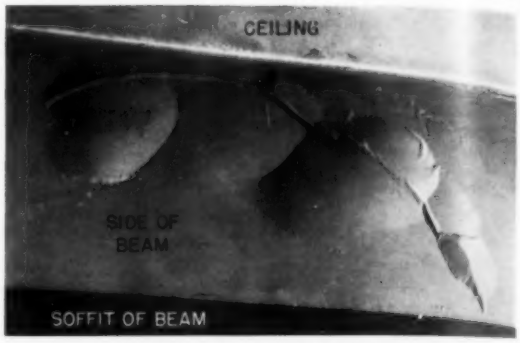


FIGURE 1. *Bulges in white coat along the side of a concrete beam, caused by the expansion attending the slow hydration of free* MgO *present in the hydrated lime used in preparing the white coat.*

FIGURE 2. *Bulging of white coat on a side wall, involving separation of the finish (or white) coat from the sanded gypsum base coat within an area of about 1 sq yd.*

## II. Scope

To procure a fair cross section of the structural hydrated limes being produced in the United States, 80 samples representing the different types were obtained from several widely separated lime-producing centers.

Because there is no satisfactory test procedure

for ascertaining volume-change characteristics of hydrated limes alone, it is necessary to gage them with some cementitious material having hydraulic properties and then to determine the expansive properties of the resultant set mixture. After numerous experiments, portland cement was chosen as the most suitable gaging material.

It soon became evident that there were numerous factors that would have to be considered before the technique of testing cement-lime specimens could be developed. Among these were: The proportion of cement to hydrated lime, the preparation and curing of the specimens, and the procedure of autoclaving.

Since autoclaves and auxiliary apparatus for testing the soundness of portland cement [6] are already available in numerous testing laboratories throughout the United States, attention was directed toward developing a procedure for testing cement-lime specimens that would utilize this equipment.

Cement to lime mixtures proportioned 2:1, 1:1, and 1:2, by weight, and also a 1:1:5 cement, lime, sand mixture were tested. Studies were made of the relation of autoclave expansion values to the quantities of unhydrated oxides as determined by chemical analyses.

The reproducibility of the test results obtained by the use of the technique developed for the tests was obtained by comparing the values obtained by independent operators.

Autoclave tests were made of the effect of 17 different portland cements on the expansion characteristics of cement-lime mixtures.

A special apparatus was designed to measure the expansion of test specimens during the course of autoclaving, which facilitated studies of the effect of the rate of heating the autoclave to a given final temperature, the final temperature itself, and the duration of autoclaving.

On the basis of the techniques developed and the results obtained in this investigation, suggestions are made for a test procedure for determining the autoclave expansion of hydrated lime and the limits that appear applicable.

## III. Materials

### 1. Hydrated Limes

Samples of the 80 representative hydrated limes, in bag quantities, were received directly from the manufacturers. Upon receipt, the materials were stored in airtight containers until used.

The chemical analyses were made in accordance with Federal Specification SS–L–351 for Hydrated Lime [7, 8], and the percentage of unhydrated oxide was calculated in accordance with Proposed Amendment 1 to this specification [3, 8]. The data are recorded in table 1, columns 2 to 10, inclusive.

On the basis of the chemical analyses, the hydrated limes were classified as high-calcium, dolomitic, and magnesian. Those containing less than 5 percent of total magnesia arbitrarily were classified as high-calcium, series A; those with more than 25 percent as dolomitic, series B and C; and four limes, having between 5 and 25 percent of magnesia, as magnesian, series D. The hydrated dolomitic limes were further subdivided into "regularly hydrated," series B, where the major portion of the magnesia had been left unhydrated, and "highly hydrated," series C, where the major portion of the magnesia had been hydrated. The designation highly hydrated follows the terminology already used in a recent publication [9] and seems preferable to such terms as "autoclaved" or "pressure hydrated limes", since some of the new limes are produced by methods that do not involve steam pressures above atmospheric.

The hydrated limes in each series are arranged in table 1 by order of increasing percentage of calculated unhydrated oxides. With the exception of the highly hydrated limes 67, 68, 71, 74, 75, and 76, which were experimentally produced, all of the hydrated limes were commercially available.

The subdivision of the hydrated limes into series A, B, C, and D and the arrangement in each series by order of increasing percentage of unhydrated oxides will be maintained in subsequent tables and figures.

No distinction between "mason's" and "finishing" hydrated limes is being made in this investigation, because the kind of unsoundness characterized by an over-all increase in volume is of concern whether a lime is to be used in a mortar or in a plaster.[2]

[2] It should be emphasized that this kind of unsoundness is not to be confused with the kind resulting in the formation of small crater-like holes known as "pits" or "pops", which sometimes occur on plastered surfaces.

TABLE 1. *Chemical analysis and calculated percentage of unhydrated oxides for 80 hydrated limes, together with the percentages of linear expansion of cement-lime bars prepared with these limes in the proportion of 2 cement:1 lime; 1 cement:1 lime; and 1 cement:2 lime, by weight, and subsequently autoclaved at a steam-gage pressure of 295 lb/in.² for 3 hr*

[The specimens were all prepared with cement 10, which, without the addition of hydrated lime, had a linear expansion of 0.11 percent]

| Lime number | Chemical analysis (oxide composition) | | | | | | | | Calculated unhydrated oxides | Linear expansion cement-lime bars in the proportion: | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Free $H_2O$ | Combined $H_2O$ | $CO_2$ | $SiO_2$ | $R_2O_3$ | CaO | MgO | Total | | 2 C:1 L | 1 C:1 L | 1 C:2 L |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
| | | | | | | SERIES A—HIGH-CALCIUM HYDRATED LIMES | | | | | | |
| | % | % | % | % | % | % | % | % | % | % | % | % |
| 1 | 0.57 | 23.74 | 0.51 | 0.54 | 0.20 | 73.92 | 0.46 | 99.94 | 0.0 | 0.13 | 0.18 | 1.1 |
| 2 | .41 | 23.18 | 1.58 | .58 | .38 | 72.82 | .67 | 99.62 | .0 | .12 | .19 | 1.1 |
| 3 | .24 | 23.59 | 1.02 | .44 | .32 | 73.97 | .33 | 99.91 | .0 | .12 | .16 | 0.71 |
| 4 | .36 | 23.68 | 0.56 | .60 | .42 | 73.90 | .35 | 99.87 | .0 | .12 | .15 | .56 |
| 5 | .29 | 23.90 | .39 | .50 | .30 | 73.62 | .82 | 99.82 | .0 | .10 | .13 | .24 |
| 6 | .66 | 23.42 | .99 | .56 | .14 | 73.17 | .60 | 99.54 | .0 | .12 | .20 | 1.4 |
| 7 | .59 | 23.66 | .70 | .16 | .55 | 73.65 | .69 | 100.00 | .1 | .14 | .18 | 1.0 |
| 8 | .83 | 23.26 | 1.10 | .20 | .55 | 73.47 | .72 | 100.13 | .5 | .14 | .19 | 0.90 |
| 9 | .54 | 23.26 | 0.68 | .86 | .48 | 73.31 | .81 | 99.94 | .8 | .14 | .21 | .86 |
| 10 | .54 | 22.96 | 1.56 | .42 | .24 | 73.22 | .96 | 99.90 | .8 | .16 | .21 | .69 |
| 11 | .53 | 23.06 | 0.70 | .74 | .60 | 72.60 | 1.04 | 99.27 | 1.0 | .14 | .19 | 1.5 |
| 12 | .29 | 23.00 | .97 | .80 | .50 | 73.29 | 0.61 | 99.46 | 1.1 | .13 | .19 | 1.3 |
| 13 | .75 | 22.95 | .67 | 1.14 | .78 | 71.35 | 1.82 | 99.46 | 1.1 | .13 | .20 | 0.78 |
| 14 | .68 | 22.58 | 1.27 | 1.02 | .64 | 71.89 | 1.19 | 99.27 | 1.2 | .13 | .18 | .59 |
| 15 | .44 | 23.07 | 0.33 | 1.09 | .50 | 72.78 | 1.06 | 99.27 | 1.6 | .12 | .18 | .97 |
| 16 | .34 | 22.88 | 1.19 | 0.58 | .38 | 73.00 | 1.41 | 99.78 | 1.7 | .16 | .23 | 1.0 |
| 17 | .58 | 22.99 | 0.65 | 1.00 | .46 | 71.55 | 2.41 | 99.64 | 1.8 | .17 | .35 | 2.0 |
| 18 | .30 | 23.23 | .27 | 0.70 | .46 | 73.68 | 1.18 | 99.82 | 2.2 | .16 | .25 | 1.3 |
| 19 | .40 | 22.20 | 1.37 | 1.88 | .92 | 72.02 | 1.09 | 99.88 | 2.3 | .13 | .24 | 1.2 |
| 20 | .33 | 22.48 | 0.87 | 0.86 | .16 | 71.23 | 3.02 | 98.95 | 3.2 | .19 | .52 | 4.1 |
| 21 | .70 | 22.01 | 1.01 | 1.31 | .76 | 72.42 | 1.29 | 99.50 | 3.9 | .17 | .24 | 1.8 |
| | | | | | | SERIES B—REGULARLY HYDRATED DOLOMITIC LIMES | | | | | | |
| 22 | 0.36 | 20.70 | 0.99 | 1.26 | 0.66 | 44.81 | 31.12 | 99.90 | 16.1 | 2.5 | 8.5 | ..... |
| 23 | .19 | 18.21 | 1.64 | 1.75 | 1.07 | 45.17 | 31.83 | 99.86 | 22.1 | 7.8 | 16.5 | ..... |
| 24 | .25 | 17.51 | 2.57 | 0.82 | 0.36 | 52.58 | 25.79 | 99.88 | 22.1 | 3.3 | 9.9 | ..... |
| 25 | .30 | 19.03 | 0.45 | 1.04 | .48 | 46.14 | 32.54 | 99.98 | 22.7 | 2.0 | 7.6 | ..... |
| 26 | .35 | 18.21 | 1.32 | 1.20 | .44 | 47.51 | 30.64 | 99.67 | 22.9 | 1.3 | 4.6 | ..... |
| 27 | .30 | 17.96 | 0.63 | 0.94 | .36 | 46.72 | 33.08 | 99.99 | 25.9 | 4.1 | 10.0 | 12.7 |
| 28 | .13 | 17.90 | 1.01 | .12 | .16 | 47.41 | 33.09 | 99.82 | 26.2 | 7.2 | 12.9 | 14.4 |
| 29 | .28 | 16.63 | 3.13 | .20 | .18 | 46.98 | 32.51 | 99.91 | 26.2 | 4.6 | 9.2 | 13.1 |
| 30 | .28 | 17.58 | 1.18 | .28 | .22 | 47.58 | 32.62 | 99.74 | 26.4 | 4.0 | 8.3 | 12.0 |
| 31 | .22 | 17.41 | 1.73 | .14 | .14 | 47.00 | 33.30 | 99.94 | 26.5 | 4.5 | 10.5 | ..... |
| 32 | .15 | 16.63 | 2.79 | .26 | .16 | 46.81 | 32.93 | 99.73 | 26.8 | 6.3 | 11.8 | 13.6 |
| 33 | .29 | 16.99 | 1.45 | .34 | .30 | 47.21 | 32.51 | 99.09 | 27.1 | 5.7 | 17.3 | ..... |
| 34 | .20 | 17.01 | 1.79 | .40 | .28 | 47.06 | 33.24 | 99.98 | 27.4 | 4.0 | 10.0 | 15.6 |
| 35 | .20 | 17.26 | 0.88 | .34 | .22 | 47.43 | 32.98 | 99.31 | 27.7 | 10.5 | 16.4 | 16.5 |
| 36 | .19 | 17.25 | .50 | .54 | .48 | 47.29 | 33.53 | 99.78 | 28.5 | 9.3 | 16.9 | ..... |
| 37 | .24 | 16.94 | .94 | .20 | .18 | 47.43 | 33.97 | 99.90 | 29.3 | 2.6 | 7.1 | 10.6 |
| 38 | .04 | 16.56 | .98 | .20 | .10 | 48.43 | 32.98 | 99.29 | 29.9 | 12.6 | 17.7 | ..... |
| 39 | .21 | 15.96 | 2.09 | .14 | .10 | 47.76 | 33.69 | 99.95 | 30.4 | 6.8 | 11.7 | ..... |
| 40 | .17 | 16.65 | 0.90 | .20 | .12 | 47.83 | 34.10 | 99.97 | 30.4 | 11.0 | 13.8 | 14.5 |
| 41 | .23 | 16.53 | 1.02 | .24 | .12 | 47.79 | 34.06 | 99.99 | 30.5 | 10.4 | 13.5 | 14.2 |
| 42 | .16 | 15.97 | 1.59 | .37 | .53 | 48.45 | 33.05 | 100.12 | 30.7 | 5.1 | 12.7 | ..... |
| 43 | .20 | 16.29 | 1.31 | .18 | .16 | 47.85 | 34.01 | 100.00 | 30.8 | 6.6 | 12.2 | 13.6 |
| 44 | .22 | 16.28 | 0.75 | .80 | .54 | 47.63 | 33.63 | 99.85 | 30.8 | 8.0 | 15.8 | 17.9 |
| 45 | .43 | 15.81 | 1.45 | .10 | .12 | 46.78 | 35.21 | 99.90 | 32.1 | 4.0 | 9.9 | 10.7 |
| 46 | .04 | 15.91 | 1.05 | .14 | .18 | 48.32 | 34.30 | 99.94 | 32.5 | 11.7 | 17.8 | ..... |
| 47 | .30 | 15.45 | 0.79 | 1.42 | .46 | 47.70 | 33.82 | 99.94 | 32.8 | 6.5 | 14.1 | ..... |
| 48 | .50 | 14.58 | 1.25 | 1.34 | .68 | 48.27 | 33.00 | 99.62 | 34.3 | 8.1 | 17.8 | ..... |

TABLE 1. *Chemical analysis and calculated percentage of unhydrated oxides for 80 hydrated limes, together with the percentages of linear expansion of cement-lime bars prepared with these limes in the proportion of 2 cement:1 lime; 1 cement:1 lime; and 1 cement:2 lime, by weight, and subsequently autoclaved at a steam-gage pressure of 295 lb/in.² for 3 hr*—Continued

[The specimens were all prepared with cement 10, which, without the addition of hydrated lime, had a linear expansion of 0.11 percent]

| Lime number | Chemical analysis (oxide composition) | | | | | | | | Calculated unhydrated oxides | Linear expansion cement-lime bars in the proportion: | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Free $H_2O$ | Combined $H_2O$ | $CO_2$ | $SiO_2$ | $R_2O_3$ | CaO | MgO | Total | | 2 C:1 L | 1 C:1 L | 1 C:2 L |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
| | SERIES C—HIGHLY HYDRATED DOLOMITIC LIMES | | | | | | | | | | | |
| | % | % | % | % | % | % | % | % | % | % | % | % |
| 49 | 0.04 | 25.41 | 1.44 | 1.06 | 0.52 | 41.87 | 29.45 | 99.79 | 1.4 | 0.18 | 0.25 | 0.85 |
| 50 | .21 | 25.28 | 1.72 | 0.24 | .18 | 42.58 | 29.75 | 99.96 | 2.2 | .21 | .30 | ..... |
| 51 | .16 | 25.52 | 1.32 | .23 | .35 | 43.01 | 29.65 | 100.24 | 2.3 | .26 | .42 | 3.1 |
| 52 | .00 | 25.41 | 1.33 | .26 | .36 | 42.47 | 29.88 | 99.71 | 2.3 | .21 | .31 | 1.3 |
| 53 | .51 | 24.56 | 1.87 | 1.56 | .50 | 41.83 | 29.09 | 99.92 | 2.6 | .26 | 1.1 | 5.8 |
| 54 | .04 | 25.31 | 1.56 | 0.18 | .18 | 42.59 | 30.08 | 99.94 | 2.6 | .22 | 0.36 | 2.2 |
| 55 | .16 | 25.15 | 1.36 | .20 | .20 | 42.70 | 29.57 | 99.34 | 2.7 | .23 | .48 | 1.9 |
| 56 | .24 | 25.22 | 0.66 | 1.66 | .56 | 41.99 | 29.71 | 100.04 | 2.9 | .21 | .29 | 1.9 |
| 57 | .09 | 25.14 | 1.75 | 0.26 | .10 | 42.68 | 30.04 | 100.06 | 2.9 | .25 | .37 | 2.1 |
| 58 | .02 | 24.77 | 1.16 | 1.98 | .70 | 42.06 | 29.23 | 99.92 | 3.0 | .25 | .33 | 1.4 |
| 59 | .17 | 24.47 | 2.79 | 0.18 | .14 | 42.49 | 29.75 | 99.99 | 3.0 | .24 | .36 | 2.0 |
| 60 | .17 | 24.87 | 1.12 | 1.53 | .62 | 41.95 | 29.68 | 99.94 | 3.2 | .24 | .50 | 2.5 |
| 61 | .23 | 24.58 | 1.98 | 0.18 | .16 | 42.91 | 29.14 | 99.18 | 3.2 | .22 | .31 | 0.95 |
| 62 | .25 | 24.37 | 2.00 | 1.45 | .62 | 42.10 | 29.46 | 100.25 | 3.4 | .22 | .40 | 3.3 |
| 63 | .17 | 25.18 | 0.37 | 1.82 | .44 | 42.12 | 29.82 | 99.92 | 3.4 | .22 | .36 | ..... |
| 64 | .09 | 25.67 | .38 | 0.14 | .08 | 43.22 | 30.17 | 99.75 | 3.5 | .24 | .50 | 3.6 |
| 65 | .19 | 23.66 | 3.12 | .16 | .20 | 42.78 | 29.99 | 99.20 | 4.0 | .22 | .31 | 0.65 |
| 66 | .08 | 24.82 | 0.87 | .02 | .19 | 43.41 | 30.24 | 99.63 | 5.1 | .34 | 1.2 | 5.6 |
| 67 | .16 | 23.59 | 2.30 | 1.28 | .48 | 42.37 | 29.58 | 99.76 | 5.2 | .41 | 2.6 | 9.0 |
| 68 | .14 | 22.40 | 3.31 | 1.64 | .64 | 42.13 | 29.43 | 99.69 | 6.6 | .38 | 2.4 | 8.4 |
| 69 | .09 | 22.72 | 3.40 | 0.22 | .16 | 42.89 | 29.93 | 99.41 | 6.8 | .73 | 5.1 | 8.9 |
| 70 | .20 | 23.35 | 1.18 | 2.18 | .89 | 42.89 | 29.43 | 100.12 | 6.9 | .88 | 7.1 | 11.2 |
| 71 | .07 | 22.41 | 3.75 | 0.14 | .30 | 43.02 | 30.18 | 99.87 | 7.5 | .54 | 5.2 | ..... |
| 72 | .13 | 23.83 | 1.06 | .20 | .12 | 43.73 | 30.58 | 99.65 | 7.7 | .63 | 3.3 | 8.5 |
| 73 | .09 | 23.58 | 0.91 | .14 | .26 | 44.15 | 30.84 | 99.97 | 9.0 | .82 | 5.6 | 9.1 |
| *745 | .30 | 20.20 | 2.83 | 4.48 | .76 | 41.66 | 29.40 | 99.63 | 11.6 | .48 | 2.8 | 8.8 |
| *776 | .28 | 20.65 | 2.64 | 3.44 | .72 | 42.30 | 29.91 | 99.94 | 11.7 | .55 | 3.2 | 8.3 |
| | .15 | 20.98 | 3.35 | 0.28 | .20 | 44.03 | 30.97 | 99.96 | 12.6 | 1.7 | 7.1 | 8.2 |
| | SERIES D—MAGNESIAN HYDRATED LIMES | | | | | | | | | | | |
| 77 | 0.38 | 21.67 | 0.67 | 2.26 | 0.82 | 67.78 | 6.24 | 99.82 | 5.9 | 0.19 | 0.50 | 3.6 |
| 78 | .39 | 21.92 | .96 | 0.76 | .78 | 62.96 | 11.88 | 99.65 | 7.2 | .22 | .39 | 1.1 |
| *79 | .99 | 17.69 | 4.95 | 2.47 | 3.13 | 64.61 | 6.25 | 100.00 | 9.8 | .22 | .54 | 4.6 |
| *80 | .52 | 19.79 | 1.10 | 2.64 | 1.30 | 57.13 | 16.88 | 99.36 | 12.7 | .28 | .70 | 2.8 |

* Failed to meet the requirement of Federal Specification SS–L–351 that the total CaO plus MgO shall be not less than 95%, calculated on nonvolatile basis.

## 2. Cements

Seventeen brands of portland cement were used in the investigation. The cements conformed to Federal Specification SS–C–192, Type 1 [10].

The autoclave expansions of the cements alone were determined in accordance with a test that had been adopted as standard [6] and are listed in table 2.

TABLE 2. *Autoclave expansion of 1- by 1- by 10-in. neat specimens of portland cement for determination of soundness of portland cement* [1]

| Cement number | Linear expansion | Cement number | Linear expansion | Cement number | Linear expansion |
|---|---|---|---|---|---|
| | % | | % | | % |
| 1 | 0.00 | 7 | 0.06 | 13 | 0.18 |
| 2 | .01 | 8 | .07 | 14 | .19 |
| 3 | .02 | 9 | .11 | 15 | .23 |
| 4 | .04 | 10 | .11 | 16 | .27 |
| 5 | .04 | 11 | .11 | 17 | .30 |
| 6 | .04 | 12 | .17 | | |

[1] Standard method of test for autoclave expansion of portland cement, ASTM Designation: C151–43, ASTM Standards, part II, 14 (1946); also American Association State Highway Officials Standard AASHO No. T107–45; as well as Federal Specification SS–C–158b–46 for Cement, Hydraulic; General Specifications (methods for sampling, inspection, and testing) [6].

## 3. Sand

The sand used in the preliminary tests on cement-lime-sand mortars was natural silica sand from Ottawa, Ill., graded to pass a No. 20 sieve and be retained on a No. 30 sieve. It conformed to Federal Specification SS–C–158b, paragraph F–51 [11].

# IV. Preparation and Curing of Test Specimens

All mixtures were prepared and all tests were performed in a laboratory in which the temperature was maintained at 21° ±1° C (70° ±2° F), and the relative humidity at 55 ±5 percent. The atmosphere of the moist closet was maintained at the same temperature as the laboratory and at a relative humidity of 95 ±3 percent.

The cement-lime test specimens, in the several series of tests, were proportioned by dry weight, namely, 300 g of cement to 300 g of lime, 200 g of cement to 400 g of lime, and 500 g of cement to 250 g of lime; hereafter designated as 1C:1L, 1C:2L, and 2C:1L, respectively. A limited number of mortar specimens was proportioned by dry weight in the ratio of 150 g of cement to 150 g of lime to 750 g of sand; hereafter designated as 1C:1L:5S. These quantities in each case were sufficient for the preparation of two test specimens.

To prepare cement-lime bars suitable for autoclaving, it was found necessary to modify the method used for making portland cement bars as given in Federal Specification SS–C–158b.

In the preparation of the cement-lime bars, the weighed amounts of cement and lime were shaken vigorously in a 2-qt jar until the mixture appeared uniform. The dry mix was spread on a smooth, nonabsorbent, noncorrosive plate and trowelled until visible agglomerates of lime were dispersed. Then, after collection of the material into a truncated cone, an inner and outer crater were formed in the dry mix with the end of the handle of a trowel.

For the remainder of the operation, the hands were protected with rubber gloves. During an interval of 2 min, (1) a measured quantity of clean water (temperature 21° ±1.7° C) was added; (2) the dry material was folded over the exposed surface of the water; and (3) the dry material was cut into the water with the edge of a trowel. The mix was worked by kneading, squeezing, and pounding for an additional period of 3 min. The mass was then allowed to stand undisturbed for 1 min and finally vigorously reworked for 1 min.

The above procedure was found necessary because of the difficulty in wetting cement-lime mixes and the tendency on the part of the operator to add excessive quantities of mixing water to most cement-lime mixes. By following these modifications, many mixes that at first appeared too dry eventually acquired the desired consistency by the vigorous working. The advantages of this procedure were twofold: (1) The quantity of mixing water could be reduced, and consequently the breakage of the bars resulting from shrinkage during curing was almost wholly eliminated, and (2) the quantity of water required by different limes of the same type was, with few exceptions, reduced to a narrow range.

Following completion of mixing, the Vicat penetration was determined according to the procedure given in Federal Specification SS–C–158b [6], paragraph F–47. Although the procedure for testing portland cement requires a Vicat penetration of 10 ±1 mm, it was found that this range was too narrow for cement-lime specimens for easy repro-

ducibility. Since it was found that small differences in consistency did not materially affect the expansion of the cement-lime specimens, the range was extended to 10 ±5 mm. In a few instances specimens were used even though the penetrations were not within this range, generally because there was insufficient material to prepare additional specimens.

Immediately after the determination of the Vicat penetration, the entire supply of putty was remixed for approximately 15 sec. The remixed cement-lime putty was then molded into autoclave bar molds according to the procedure given in SS–C–158b, paragraph F–61. The bar molds provided for test specimens having a cross section 1 in. by 1 in. and of 10-in. effective gage length, SS–C–158b, paragraph F–43 [6].

Immediately after molding each specimen, its exposed surface was covered with a strip of waxed paper pressed down on the mold. This waxed paper reduced surface evaporation and minimized the breakage, during curing, caused by shrinkage cracks. The test specimens were stored in the molds in a moist closet for at least 20 hrs, following the requirements of SS–C–158b, paragraph F–62.

The cement-lime-sand mortars were prepared in accordance with Federal Specification SS–C–181b [12], considering the mixture of cement and lime as masonry cement. The consistency of all mortars was adjusted to a flow of 110 ±2. The casting of the mortar into autoclave bar molds and subsequent treatment were similar to that of the cement-lime putties.

At 23 ±1 hr after molding the specimens, they were removed from the moist closet, measured for length, and placed in the autoclaves at room temperature. The autoclaves were immediately closed, and heat was applied.

After autoclaving, the specimens for the most part were submerged in water and cooled to 21° C before measuring the length, as required in the procedure of autoclaving as given in Federal Specification SS–C–158b, paragraph F–63f [6]. It was found necessary, however, to cool those specimens that exhibited very high expansions (10% or more) in air to 21° C, because when cooled in water the greatly expanded specimens were apt to disintegrate.

For expansions under 2.5 percent, the comparator described in paragraph F–45 of SS–C–158b [6] was used. For higher expansions, methods giving values to within a hundredth of an inch were used.

## V. Autoclaves and Methods of Autoclaving

Four autoclaves were used in this investigation—one, horizontal, gas-fired; and three, vertical, electrically heated. One of the latter was equipped with a special device for the continuous observation of the expanding bar specimens.

### 1. Horizontal Gas-Fired Autoclave

The detailed description of the horizontal, gas-fired autoclave will be omitted because it was not used in this investigation after it was found that the expansions obtained with it were somewhat erratic and did not agree well with the concordant results obtained with the three vertical autoclaves that were electrically heated.

It was found, for example, that the cement-lime specimens placed in the upper part of the chamber of the gas-fired autoclave expanded more than companion specimens placed in the lower part. It is believed that the reason for this is the tendency for the steam to become superheated in the upper portion of a horizontal autoclave that is gas-fired.

### 2. Vertical, Electrically Heated Autoclaves

The three electrically heated autoclaves were of such a design that they met the requirements of Federal Specification SS–C–158b [6] for an autoclave to be used in the testing of portland cement. Since preliminary experiments showed that the rate of heating cement-lime specimens markedly affected the resultant expansion of the bars, the rate of heating each autoclave to 295 lb/in.$^2$ was determined. It can be seen from figure 3 that with each autoclave the pressure of the saturated steam in the autoclave was raised to a gage pressure of 295 lb/in.$^2$ in 1 to 1¼ hr, as required by the standard method for testing cement [6].

Autoclaves designated as 1 and 2 were used in the preliminary experiments wherein the cement-lime and cement-lime-sand specimens were autoclaved at gage pressures of 25, 120, and 295 lb/in.$^2$ and also in the bulk of the work where the autoclaving was done in accordance with the standard method for portland cement specimens (295 lb/in.$^2$).

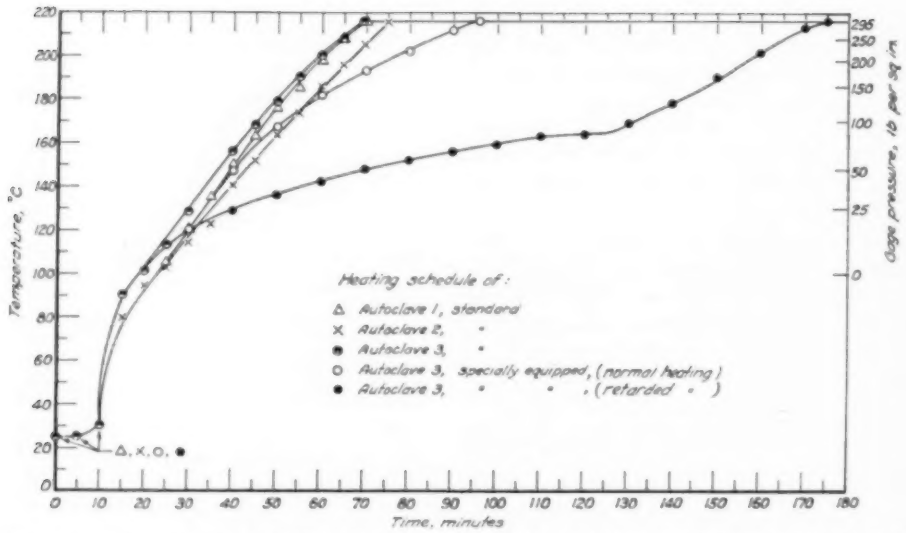
Temperature, °C
Gage pressure, lb per sq in.
Time, minutes
Heating schedule of:
Autoclave 1, standard
Autoclave 2, "
Autoclave 3, "
Autoclave 3, specially equipped, (normal heating)
Autoclave 3, " " , (retarded " )
Δ, ×, ○, ●

FIGURE 3. *Time-temperature curves of heating autoclaves to 216° C (equivalent to steam-gage pressure of 295 lb/in.²).*

The method of autoclaving at 295 lb/in.² was used in accordance with ASTM and Federal Specifications for testing portland cement. When the autoclaving was done at 25 and 120 lb/in.², the heating schedule of the standard autoclaves 1 and 2 (fig. 3) was followed to the required pressure, after which the pressure, or temperature, was maintained by manual control.

### 3. Special Autoclave for Continuous Observation of Expansion[3]

Figure 4 shows the apparatus that permitted continuous observation of the expansion of a bar (cement or cement-lime specimens) during the course of autoclaving. Figure 5 is a schematic drawing of the specially equipped, electrically heated autoclave illustrated in figure 4. The device consisted of a high-pressure gage-glass chamber, A, mounted on top of autoclave 3 by means of a short length of threaded high-pressure pipe screwed into a threaded hole tapped through the cover plate of the autoclave. A free-moving square steel rod, B, extended from the inside of the autoclave through the connecting pipe into the gage-glass chamber. The top of the rod was pointed in order to serve as a reference. The lower end, which extended through the connecting pipe into the autoclave chamber, was provided with a steel disk, K, that rested on the top of the test specimen, H, which was held vertically in a rack, R, placed in the chamber of the autoclave. With this arrangement, an expanding test bar caused the steel rod to rise in the gage-glass chamber, and the movement could be observed by sighting through the parallel glass windows of the chamber. By having the rod square, passage of steam and condensed water in and out of the gage-glass chamber was assured. A small steel spring, I, was attached to one side of the steel rod to prevent the rod from falling out of the gage-glass chamber while the cover plate was being placed and removed.

It was found that bars that were being continuously wetted during autoclaving gave erratic and unusually large expansions. Therefore, it was necessary to divert condensed dripping water away from the test specimen located directly below the gage-glass chamber, and hence a copper flashing, J, (fig. 5) was attached to the movable square steel rod directly above the steel disk that rested on the top of the specimen. As a check on the performance of the test bar carrying the movable steel rod, a duplicate bar was always placed in the same autoclave away from the dripping condensed water; after autoclaving, both bars were measured with a comparator.

In operation, the test bar was placed in a rack

[3] Special acknowledgment is due Emil Trattner for his graciousness in consenting to the description of his ingeneously designed autoclave, which permitted, for the first time, the observation of a test specimen during the course of autoclaving.

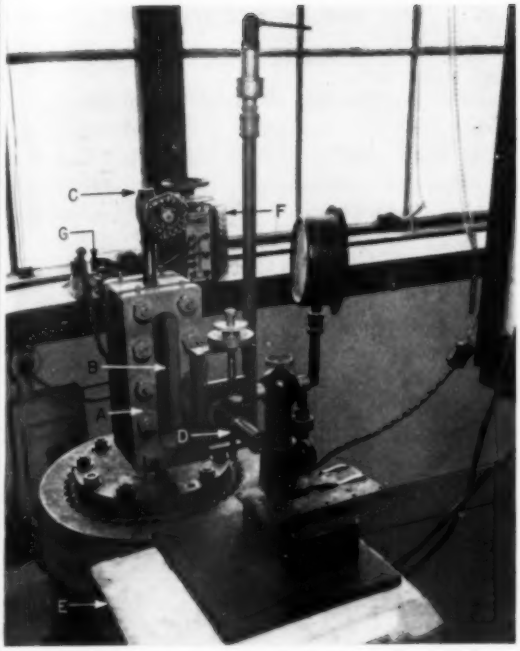


FIGURE 4. *Assembly of specially equipped autoclave for continuous observation of expanding bar-specimens during autoclaving.*

A, Gage-glass chamber mounted on top of autoclave; B, movable square steel rod extending from top of specimen into the gage-glass chamber; C, vent valve; D, cathetometer for measuring movement of movable steel rod; E, stone base for cathetometer; F, variac; G, voltmeter.

in the autoclave, and the cover plate with the attached gage-glass chamber, together with the inserted steel rod held in place by the restricting spring, was lowered into place in such a manner that the steel disk at the lower end of the rod came to rest on the flat top of the test bar.[4] The cover plate was then bolted down and the vent valve, C, was opened.

The position of the point of the free-moving steel rod was located by means of the cathetometer, D, (fig. 4), which was firmly mounted on a stone base, E.

The heaters were then turned on, and the water in the bottom of the autoclave was brought to boiling. After the air had been displaced by steam, the vent valve, C, was closed. The autoclave was heated to a final pressure of 295 lb/in.$^2$, at which pressure the thermometer reading was 216° C. The rate of heating was controlled

[4] The steel reference point that normally would be present at the top of the test bar, for measurement with a comparator, had been removed during fabrication.

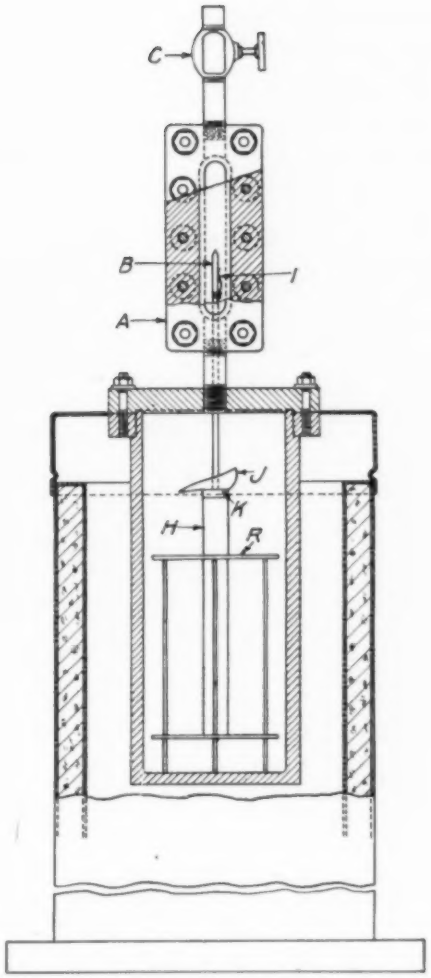


FIGURE 5. *Details of gage-glass chamber and movable steel rod.*

A, Gage-glass chamber; B, movable square steel rod; C, vent valve; H, bar-specimen; I, spring for holding movable square steel rod in place while assembling apparatus; J, copper flashing attached to movable steel rod to divert condensing water running down rod away from specimen H; K, steel disk attached to lower end of movable steel rod and resting on top of specimen; R, rack for holding specimen upright.

manually by means of the several heating units of the autoclave. A variac, F, connected through a voltmeter, G, added flexibility to the control.

Readings of the position of the rising steel rod were obtained easily until the vent was closed. Immediately thereafter, readings could not be taken with the cathetometer because of the condensation of drops of water on the inside of the glass windows of the gage-glass chamber. This

condition lasted for about 1 or 2 min. However, since the gage-glass chamber acted as a condenser, the interior soon became completely filled with water.[5] From then on, the point of the steel rod was clearly visible.

The shortest time within which the gage pressure could be raised to 295 lb/in.$^2$ was about 97 min., compared to the 70 min. required to heat the same autoclave without the gage-glass chamber. This 97 min. is beyond the upper limit of 1¼ hr specified in SS–C–158b [6]. The increase in time was caused by the greater heat input required by the condensing and refluxing of the water in the gage-glass chamber and by the greater heat capacity of the specially equipped autoclave. The normal heating schedule of specially equipped autoclave 3 is shown in figure 3.

Throughout the entire course of autoclaving, readings were taken of the position of the point of the moving steel rod with the cathetometer, of the pressure with the steam gage, and of the temperature with a thermometer inserted into a thermometer well in the cover plate.

The design of the apparatus was such that thermal expansions were included in the measurements. The thermal expansions of concern were those of the free-moving steel rod, the test bar, and the part of the autoclave below the lower end of the test bar. This combined thermal expansion was determined by inserting a test specimen that had previously been autoclaved at a gage pressure of 295 lb/in.$^2$, setting up the equipment as in a normal test procedure, and heating to 295 lb/in.$^2$. The movement of the point of the steel rod was observed and taken as the thermal expansion of the combined parts. The previously autoclaved test bar used in this experiment was measured with a comparator before and after autoclaving and was found to have shown no subsequent expansion. These results were checked by replacing the cement-lime test bar with a steel bar of equal length and of known coefficient of expansion. The magnitude of the thermal expansion compared with the observed total expansion of the test specimens will be discussed later.

[5] To compensate for water condensed in the gage-glass chamber, 500 ml of water, rather than the usual 500 ml, was placed in this special autoclave at the start.

## VI. Results and Discussion

### 1. Preliminary Experiments

Table 3 gives data on some preliminary experiments on the expansion of cement-lime and cement-lime-standard sand specimens that were autoclaved at steam-gage pressures of 25, 120, and 295 lb/in.$^2$, respectively. It can be seen that, without exception, increasing the pressure of autoclaving from 25 to 120 to 295 lb/in.$^2$ was attended by an increase in the percentage of the linear expansion.

Also, increasing the proportion of lime to cement from 2C:1L to 1C:1L invariably resulted in a marked increase in expansion at each pressure of autoclaving. Increasing the proportion of lime in the cement-lime specimens results in a decrease in the strength of the specimen and therefore a decrease in the ability of the specimen to resist expansive forces. It is believed that an increase in expansion attending a decrease in the strength accounts for the relatively high expansion values of the 1C:1L:5S group. In fact, the weakness of the sanded bars and the difficulty of their preparation and handling discouraged further work with sanded specimens. In addition, the possibility of a variable being introduced because of a probable pozzolanic reaction between the lime and sand during autoclaving further operated against their use.

Figure 6 shows the increase in expansion at-

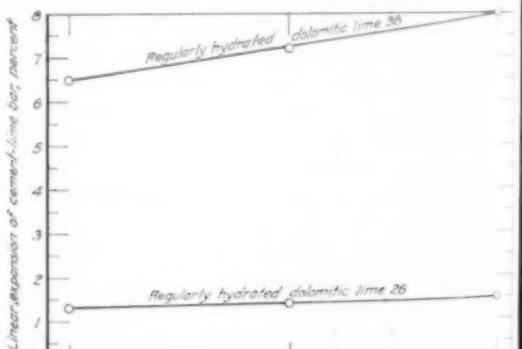


FIGURE 6. *Increase in expansion of cement-lime bars attending increase in time of autoclaving at gage-pressure of 25 lb/in.$^2$.*

TABLE 3. *Expansion of cement-lime and cement-lime-standard sand bars autoclaved at steam-gage pressures of 25, 120, and 295 lb/in.² for 3 hr, respectively*

[Cement 10 was used throughout]

| Lime Number | Type of lime | Unhydrated oxides | Mixing water | Vicat penetration | Flow | Linear expansion after autoclaving at pressures of— | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | 25 lb/in.² | 120 lb/in.² | 295 lb/in.² |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| GROUP 1. PROPORTION OF CEMENT:LIME—2:1, BY WEIGHT | | | | | | | | |
| | | % | % | *mm* | % | % | % | % |
| 26 | (a) | 22.9 | 34 | 8 | ..... | 0.40 | 0.93 | 1.3 |
| 33 | (a) | 27.1 | 34 | 11 | ..... | 1.5 | 4.6 | 5.7 |
| 38 | (a) | 29.9 | 35 | 8 | ..... | 3.9 | 9.6 | 12.6 |
| 39 | (a) | 30.4 | 34 | 10 | ..... | 2.1 | 5.6 | 6.8 |
| 55 | (b) | 2.7 | 34 | 10 | ..... | 0.10 | 0.13 | 0.23 |
| 58 | (b) | 3.0 | 29 | 9 | ..... | .06 | .09 | .25 |
| 60 | (b) | 3.2 | 31 | 10 | ..... | .07 | .10 | .24 |
| 69 | (b) | 6.8 | 31 | 8 | ..... | .23 | .51 | .73 |
| GROUP 2. PROPORTION OF CEMENT:LIME—1:1, BY WEIGHT | | | | | | | | |
| 26 | (a) | 22.9 | 40 | ..... | ..... | 1.3 | 3.9 | 4.6 |
| 33 | (a) | 27.1 | 40 | ..... | ..... | 7.7 | 11.6 | 17.3 |
| 38 | (a) | 29.9 | 42 | ..... | ..... | 6.5 | 14.7 | 17.7 |
| 39 | (a) | 30.4 | 41 | ..... | ..... | 4.8 | 9.3 | 11.7 |
| 55 | (b) | 2.7 | 43 | ..... | ..... | 0.15 | 0.26 | 0.48 |
| 58 | (b) | 3.0 | 34 | ..... | ..... | .08 | .16 | .33 |
| 60 | (b) | 3.2 | 34 | ..... | ..... | .10 | .22 | .50 |
| 69 | (b) | 6.8 | 36 | ..... | ..... | 1.3 | 3.4 | 5.1 |
| GROUP 3. PROPORTION OF CEMENT:LIME:SAND—1:1:5, BY WEIGHT | | | | | | | | |
| 26 | (a) | 22.9 | 15.8 | ..... | 109 | 0.72 | 2.4 | 4.0 |
| 33 | (a) | 27.1 | 15.8 | ..... | 108 | 4.7 | 7.5 | 9.0 |
| 38 | (a) | 29.9 | 14.8 | ..... | 108 | 7.0 | 11.6 | 13.0 |
| 39 | (a) | 30.4 | 15.6 | ..... | 112 | 4.5 | 7.5 | 8.8 |
| 55 | (b) | 2.7 | 17.5 | ..... | 108 | 0.06 | 0.10 | 0.18 |
| 58 | (b) | 3.0 | 16.2 | ..... | 108 | .05 | .08 | .16 |
| 60 | (b) | 3.2 | 18.1 | ..... | 108 | .05 | .10 | .20 |
| 69 | (b) | 6.8 | 15.2 | ..... | 110 | .56 | 2.2 | 4.0 |

[a] Regularly hydrated dolomitic lime.
[b] Highly hydrated dolomitic lime.

tending an increase in the time of autoclaving specimens containing hydrated limes (26 and 38) at a pressure of 25 lb/in². The expansion curves indicate that the ultimate expansion had not been reached after 7 hr of autoclaving. The investigation of the effect of time of autoclaving at a pressure of 25 lb/in². was not extended beyond 7 hr, because even that is too long for a continuous laboratory test procedure.

It became evident from these preliminary experiments that the pressure of autoclaving is an important factor with respect to the magnitude of the expansion. It is also evident that at lower pressures the total expansion is not reached within a practicable time. It was found, however, that cement-lime bars as well as portland-cement bars underwent no further expansion at 295 lb/in². when autoclaved for periods in excess of 3 hr. It was decided, therefore, to abandon further work with lower pressures and to limit all further experiments to autoclaving for 3 hr at a pressure of 295 lb/in ².

## 2. Effect of Increasing Proportion of Hydrated Lime on Expansion of Cement-Lime Bars

Table 1 (cols. 11, 12, and 13) gives data on the expansion of cement-lime bars prepared in the proportions of 2C:1L, 1C:1L, and 1C:2L,

by weight, respectively, and autoclaved for 3 hr at a gage pressure of 295 lb/in$^2$.

The values for the percentage of expansion recorded in columns 11 and 13 are averages obtained by single operators from duplicate specimens. Forty-three of the values in column 12 represent the averages for duplicate determinations of three independent operators; the remainder are the average of duplicate determinations by a single operator.

Figures 7, 8, and 9 show the respective expansions of the 2C:1L, 1C:1L, and 1C:2L bars (cols. 11, 12, and 13 of table 1), plotted against the percentages of unhydrated oxides (col. 10 of table 1) in the hydrated lime used in preparing the bars. Several salient features are evident from table 1, and figures 7, 8, and 9.

From the figures it can be seen that the limes are distributed into two major groups. One is composed entirely of the regularly hydrated dolomitic limes (series B) and is characterized by containing those limes having the highest percentage of unhydrated oxides and the highest percentage of expansion. The other group is composed of the remaining limes (series A, C, and D).

The high-calcium limes (series A) are characterized in general by having the lowest percentages of unhydrated oxides (0 to 3.9 percent) and the lowest percentages of expansion. This can best be observed from table 1.

Most of the highly hydrated dolomitic limes (series C) have percentages of unhydrated oxides (1.4 to 4.0 percent) and, with one exception, expansions that are comparable to those of the high-calcium limes. These are limes 49 to 65, inclusive, and are all commercially available limes. The others (limes 66 to 76, incl.) have percentages of unhydrated oxides (5.1 to 12.6) and expansions that are greater than those of the high-calcium limes. Among these limes are 67, 68, 71, 75, and 76, which were experimentally produced.

The four magnesian limes (series D) exhibit

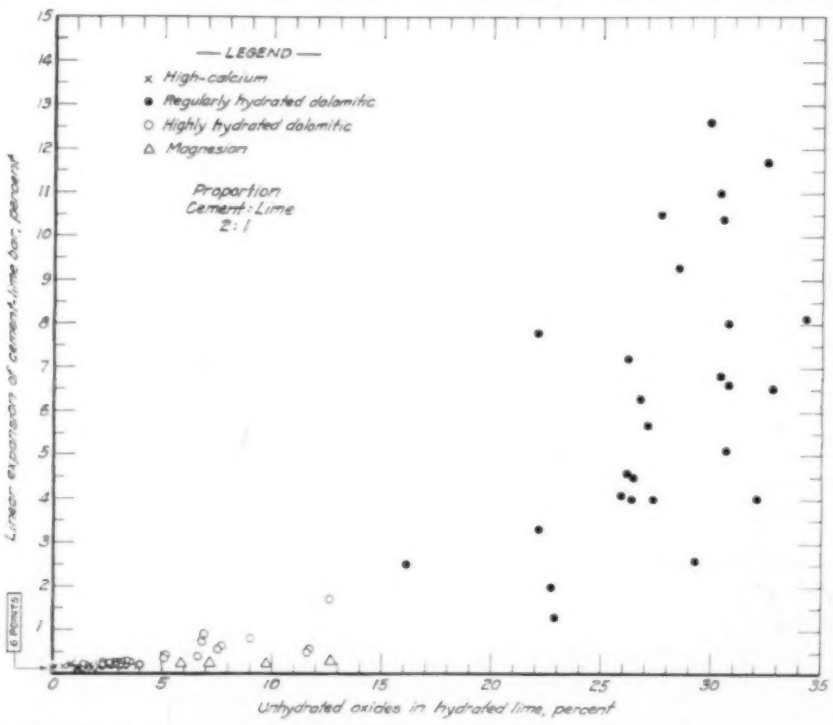


FIGURE 7. *Linear expansion of cement-lime bars prepared with hydrated limes containing various amounts of unhydrated oxides, in the proportion of 2 cement to 1 lime (by weight) and subsequently autoclaved for 3 hr at a gage pressure of 295 lb/in$^2$.*

The specimens were all prepared with cement 10, which, without the addition of hydrated lime, had a linear expansion of 0.11 percent.

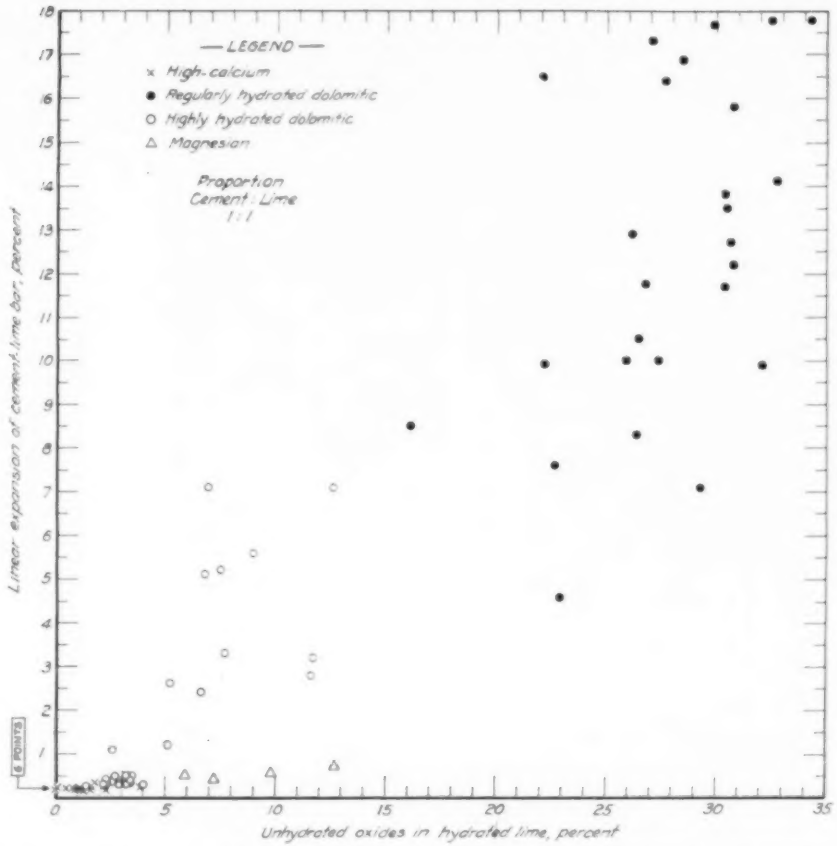


FIGURE 8. *Linear expansion of cement-lime bars prepared with hydrated limes containing various amounts of unhydrated oxides, in the proportion of 1 cement to 1 lime (by weight) and subsequently autoclaved for 3 hr at a gage pressure of 295 lb/in².*

The specimens were all prepared with cement 10, which, without the addition of hydrated lime, had a linear expansion of 0.11 percent.

unique behavior in that each magnesian lime shows a lower percentage of expansion than other limes with a comparable percentage of unhydrated oxides.

From table 1 it can be seen that, for the limes of each series, an increase in the proportion of lime in the cement-lime bars is, without exception, attended by an increase in expansion. This relation is also shown in figure 10, where the percentages of linear expansion of the 2C:1L, 1C:1L, and 1C:2L bars are plotted consecutively.

Figure 10 shows, again, that as a group the high-calcium limes give the lowest expansions in the three cement-lime proportions, and that a majority of the highly hydrated dolomitic limes give expansions comparable to the high-calcium limes. It also reveals that the expansions of the remaining 11 highly hydrated dolomitic limes, which include the six experimental limes, are intermediate between those of the high-calcium and the regularly hydrated dolomitic limes. However, in the 2C:1L proportion, the expansions of the high-calcium and all of the highly hydrated dolomitic limes fall within a narrow range—with only one exception, under 1.0 percent. As the proportion of the lime in the bar increases from 2C:1L to 1C:1L, the spread in expansion is greatly accentuated for those highly hydrated dolomitic limes having expansions beyond the range of the high-calcium limes. The spread in expansion is even more accentuated in the 1C:2L bars.

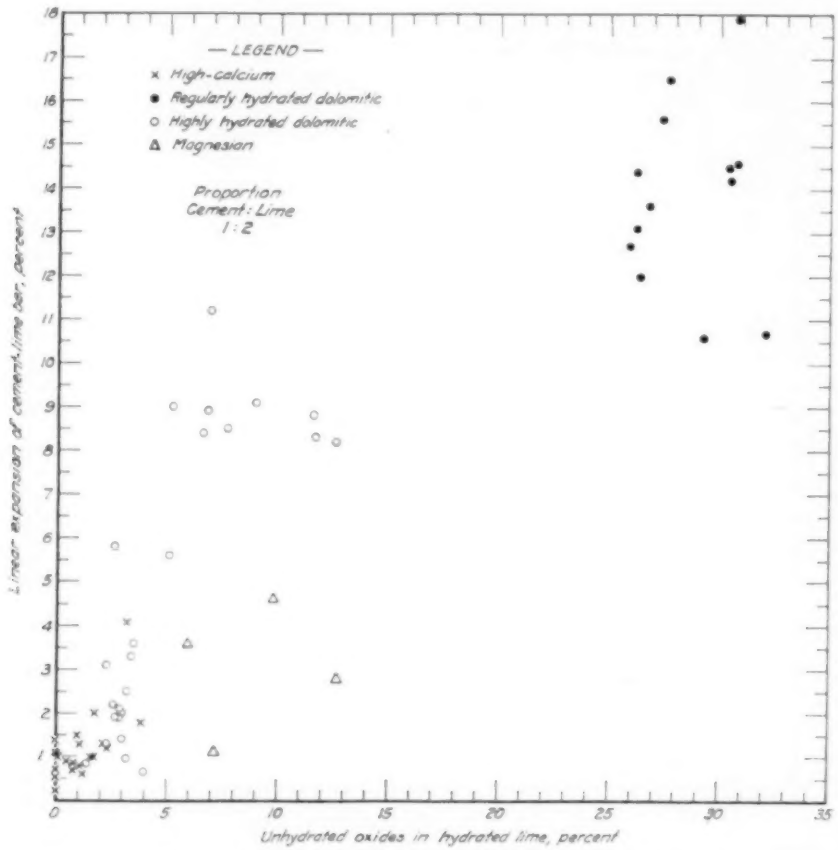


FIGURE 9. *Linear expansion of cement-lime bars prepared with hydrated limes containing various amounts of unhydrated oxides in the proportion of 1 cement to 2 lime (by weight) and subsequently autoclaved for 3 hr at a gage pressure of 295 lb/in².*

The specimens were all prepared with cement 10, which, without the addition of hydrated lime, had a linear expansion of 0.11 percent.

In figures 7, 8, and 9 the expansions of the 2C:1L, 1C:1L, and 1C:2L bars were plotted in each case against the calculated percentage of unhydrated oxide in the constituent lime. However, the percentages of unhydrated oxide in the 2C:1L, 1C:1L, and 1C:2L mixes are respectively one-third, one-half, and two-thirds of that of the percentage of unhydrated oxide in the lime. Accordingly, figure 11 shows the relation between the percentages of expansion of 2C:1L, 1C:1L, and 1C:2L bars and the corresponding percentage of unhydrated oxide in the dry mix.

Once more, it can be seen from figure 11, where the percentages of expansion of the 2C:1L, 1C:1L, and 1C:2L bars are plotted side by side, that an increase in the proportion of lime in the bars is accompanied by an increase in expansion. But more important, the three graphs making up figure 11 show that the percentage of unhydrated oxide in the mix must be low if there is to be assurance that the expansion will also be low. It is also evident that the limiting percentage is not the same for each proportion of cement to lime. This percentage apparently narrows as the quantity of cement decreases and the bars correspondingly become weaker and are less able to resist the expansive forces attending the hydration of the unhydrated oxide. For example, with the 2C:1L bars, the total unhydrated oxide may be as high as 4 percent and yet the expansion of the bars remain below 1 percent. With the weaker 1C:1L bars, the percentage of unhydrated oxide that

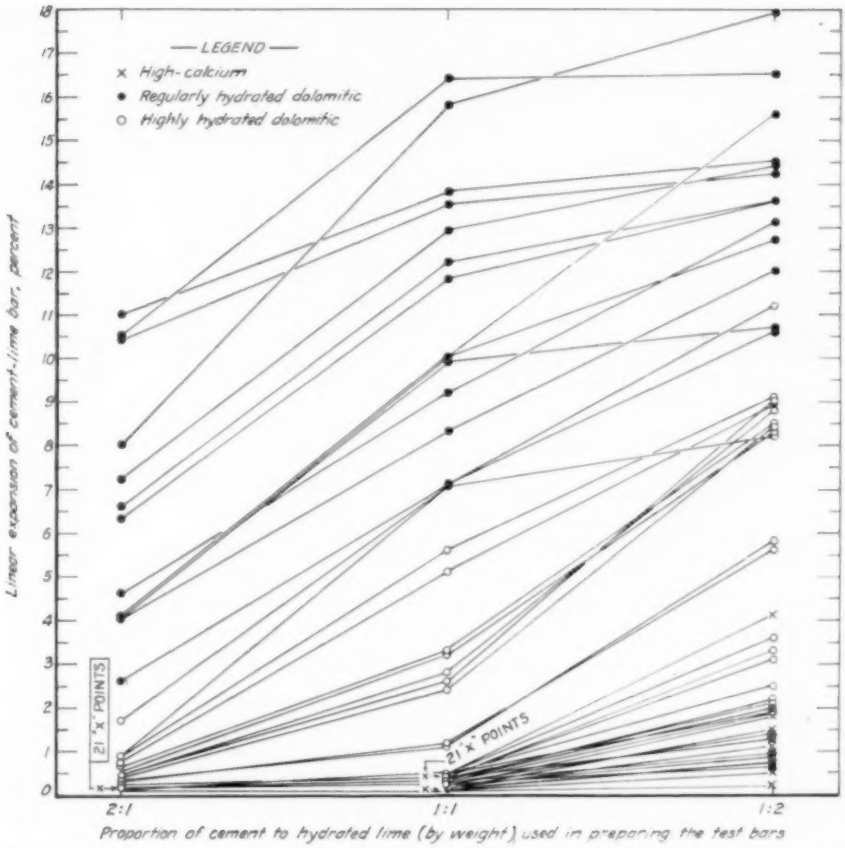


FIGURE 10. *Increase in linear expansion attending an increase in the proportion of lime in cement-lime bars autoclaved for 3 hr at a gage pressure of 295 lb/in.²*

can be tolerated appears to be less, because at 4 percent the expansion may exceed 6 percent. With the still weaker 1C:2L bars, the expansion of the bars with 4 percent of unhydrated oxide may reach values in the neighborhood of 10 percent. In fact, even with little or no unhydrated oxide, the bars of the 1C:2L series show expansions considerably greater than those of the other two mixes. It is not known whether this can be attributed in part to the cement itself because of the inability of these weak bars to resist the expansion of some of the constituents of the cement. It is interesting that the unique magnesian limes, which show less expansion than other limes with comparable percentage of unhydrated oxide, begin to show appreciable expansion in the 1C:2L bars.

### 3. Reproducibility of Determining Percentage of Expansion of 1 Cement:1 Lime Test Specimens

Table 4 gives data on the percentage of linear expansion obtained by three operators with duplicate cement-lime bars prepared in the proportion of 1 part cement to 1 part lime, by weight, and autoclaved at a steam-gage pressure of 295 lb/in.² for 3 hr. In addition, it gives for each operator the percentage of water used in fabricating the duplicate bars and the Vicat penetration of the cement-lime pastes. Forty-three samples of hydrated limes were selected for this study. In certain instances only one of an operator's duplicate bars was autoclaved.

Although the dates at which the tests were performed are not given in table 4, the experiments



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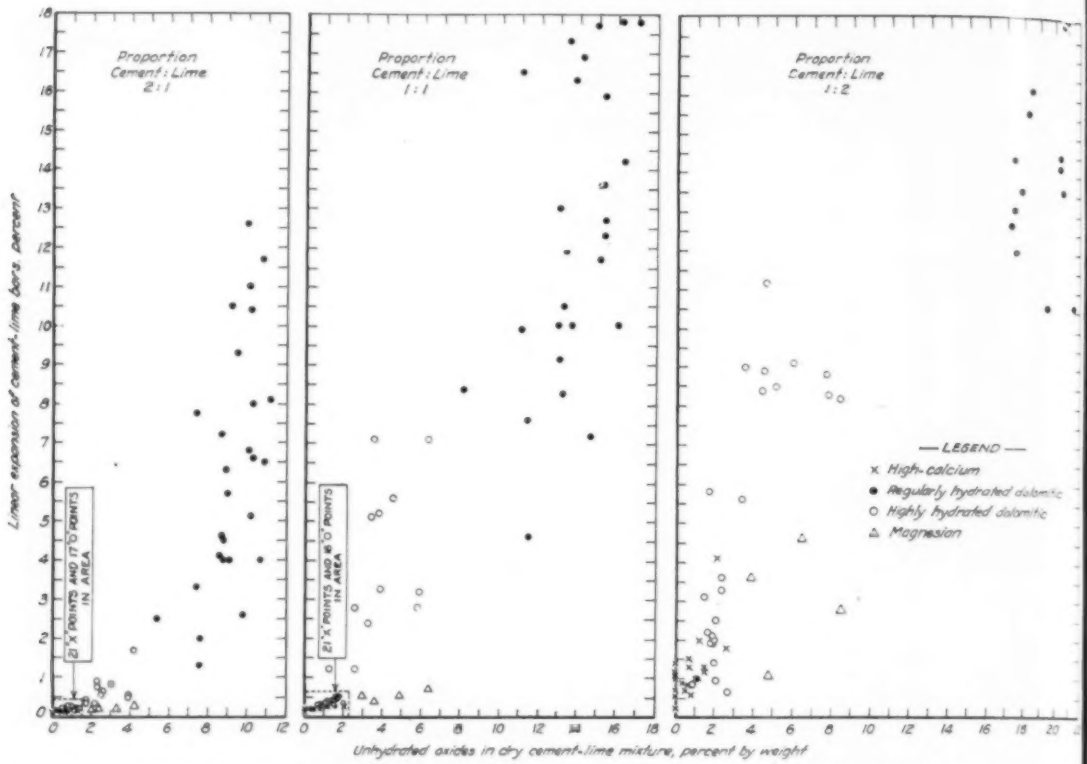
Proportion Cement: Lime 2:1
Proportion Cement: Lime 1:1
Proportion Cement: Lime 1:2
21 "X" POINTS AND 17 "O" POINTS IN AREA
21 "X" POINTS AND 16 "O" POINTS IN AREA
— LEGEND —
× High-calcium
● Regularly hydrated dolomitic
○ Highly hydrated dolomitic
△ Magnesian
Linear expansion of cement-lime bars, percent
Unhydrated oxides in dry cement-lime mixture, percent by weight

FIGURE 11. *Relation between the percentage of expansion of 2C:1L, 1C:1L, and 1C:2L bars and the corresponding percentage of unhydrated oxides in the dry mix.*

purposely were not made at the same time. The time period between the testing by operators B and C was approximately 1 month. Operator A did most of his testing about 1 year later.

It can be seen from table 4 that not only did the percentages of expansion of the two duplicate bars of each operator agree closely, but that the percentages of expansion obtained by the three different operators were in good agreement.

For the purpose of a statistical treatment, the various hydrated limes were divided into five nearly homogeneous groups. These include series A, high-calcium; series B, regularly hydrated dolomitic; series D, magnesian; and two subdivided groups of series C, highly hydrated dolomitic. One of these groups of series C included the highly hydrated dolomitic limes having percentages of both unhydrated oxide and expansion of the same order of magnitude as those of the high-calcium limes, namely, limes 49, 54, 56, 57, 59, 61, and 65, all of which had expansions of less than 0.40 percent. The other group contained the limes in series C having the high expansions those ranging from 1.1 to 5.6 percent. A single classification analysis of variance [13] was made for each group to test whether there was a significant difference among the averages obtained by the three operators. No significant difference was found.[6]

### 4. Effect of Different Portland Cements on Expansion of Cement-Lime Bars

Table 5 gives data on the expansion of cement-lime bars prepared with 17 cements (ranging in expansion from 0.00 to 0.30 percent). The 30 selected limes are grouped, as heretofore, in four series.

The values for the percentage of expansion of the 17 cements (tested in accordance with the

[6] The authors thank Stephen W. Benedict for his statistical analysis of the reproducibility of determining the percentage of expansion of cement-lime test specimens.

TABLE 4. *Reproducibility obtained, by three independent operators, for the expansion of cement-lime bars prepared in the proportion of 1 cement:1 lime (by weight), and autoclaved at a steam-gage pressure of 295 lb/sq in.² for 3 hr. The specimens were all prepared with cement 10, which, without the addition of hydrated lime, had a linear expansion of 0.11 percent*

| Lime number | Calculated unhydrated oxides | Consistency (water, percent; and Vicat penetration, mm) of cement-lime pastes as obtained by operator— | | | | | | Linear expansion of duplicate cement-lime bars as obtained by operator— | | | | | | Average of linear expansion values |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | A | | B | | C | | A | | B | | C | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| **SERIES A—HIGH-CALCIUM HYDRATED LIMES** | | | | | | | | | | | | | | |
| | % | % | *mm* | % | *mm* | % | *mm* | % | % | % | % | % | % | % |
| 1 | 0.0 | 41 | 6 | 42 | 7 | 41 | 5 | 0.18 | 0.18 | ..... | 0.18 | 0.18 | 0.20 | 0.18 |
| 2 | .0 | 44 | 11 | 44 | 9 | 43 | 9 | .18 | .18 | ..... | .20 | ..... | .20 | .19 |
| 3 | .0 | 41 | 6 | 41 | 8 | 41 | 8 | .16 | .16 | ..... | .15 | ..... | .16 | .16 |
| 4 | .0 | 42 | 5 | 41 | 6 | 42 | 7 | .16 | .16 | 0.15 | .15 | .15 | .15 | .15 |
| 5 | .0 | 38 | 14 | 38 | 10 | 38 | 12 | .14 | .14 | .13 | .13 | .13 | .13 | .13 |
| 6 | .0 | 41 | 5 | 41 | 7 | 41 | 6 | .19 | .19 | .19 | .19 | .21 | .21 | .20 |
| 11 | 1.0 | 41 | 9 | 41 | 8 | 40 | 6 | .19 | .19 | .19 | .19 | .20 | .20 | .19 |
| 13 | 1.1 | 44 | 4 | 44 | 7 | 43 | 5 | .20 | .20 | ..... | .20 | .20 | .21 | .20 |
| 14 | 1.2 | 41 | 7 | 41 | 8 | 41 | 7 | .18 | .18 | ..... | .18 | .19 | .19 | .18 |
| 15 | 1.6 | 39 | 4 | 39 | 6 | 39 | 5 | .18 | .18 | ..... | .17 | .18 | .19 | .18 |
| **SERIES B—REGULARLY HYDRATED DOLOMITIC LIMES** | | | | | | | | | | | | | | |
| 22 | 16.1 | 41 | 5 | 41 | 12 | 41 | 7 | ..... | 7.6 | 8.8 | 8.9 | ..... | 8.6 | 8.5 |
| 27 | 25.9 | 40 | ..... | 39 | 17 | 38 | 3 | 9.8 | 10.2 | 9.5 | 9.7 | 10.4 | 10.4 | 10.0 |
| 28 | 26.2 | 38 | 6 | 38 | 7 | 39 | 9 | 12.5 | 12.5 | ..... | 13.5 | ..... | 13.1 | 12.9 |
| 29 | 26.2 | 37 | 11 | 37 | 9 | 37 | 11 | 9.2 | 9.3 | 8.9 | 8.9 | 9.2 | 9.4 | 9.2 |
| 30 | 26.4 | 37 | 7 | 37 | 11 | 38 | 8 | 8.3 | 8.4 | ..... | 8.1 | 8.3 | 8.4 | 8.3 |
| 32 | 26.8 | 37 | 10 | 38 | 20 | 38 | 11 | 11.6 | 11.6 | ..... | 12.0 | ..... | 12.0 | 11.8 |
| 34 | 27.4 | 38 | 7 | 39 | 8 | 38 | 8 | 10.1 | 10.1 | ..... | 9.8 | 10.1 | 9.8 | 10.0 |
| 35 | 27.7 | 37 | 9 | 38 | 13 | 38 | 10 | 16.3 | 16.2 | 16.4 | 16.4 | 16.4 | 16.4 | 16.4 |
| 36 | 28.5 | 41 | 8 | 42 | 13 | 41 | 4 | 17.4 | 17.4 | 16.4 | 16.4 | ..... | 17.0 | 16.9 |
| 37 | 29.3 | 39 | 4 | 38 | 5 | 38 | 5 | 6.9 | 6.9 | 7.3 | 7.3 | ..... | 7.3 | 7.1 |
| 40 | 30.4 | 38 | 5 | 39 | 11 | 38 | 8 | ..... | 14.0 | ..... | 12.6 | 14.1 | 14.3 | 13.8 |
| 41 | 30.5 | 38 | 7 | 38 | 6 | 38 | 6 | ..... | 13.8 | 13.2 | 12.7 | 13.8 | 14.0 | 13.5 |
| 43 | 30.8 | 38 | 5 | 38 | 10 | 38 | 7 | 12.0 | 12.0 | ..... | 12.4 | ..... | 12.4 | 12.2 |
| 44 | 30.8 | 40 | 10 | 40 | 10 | 42 | 19 | 15.3 | 14.9 | ..... | 16.4 | 16.0 | 16.4 | 15.8 |
| 45 | 32.1 | 42 | 6 | 41 | 5 | 42 | 7 | 9.3 | 9.1 | ..... | 10.1 | 10.6 | 10.5 | 9.9 |
| 47 | 32.8 | 39 | 5 | 39 | 12 | 39 | 7 | 14.2 | 14.2 | ..... | 14.5 | 14.0 | 13.8 | 14.1 |
| **SERIES C—HIGHLY HYDRATED DOLOMITIC LIMES** | | | | | | | | | | | | | | |
| 49 | 1.4 | 35 | ..... | 39 | 5 | 40 | 10 | 0.25 | 0.26 | 0.24 | 0.25 | 0.26 | 0.25 | 0.25 |
| 53 | 2.6 | 39 | 8 | 38 | 4 | 39 | 9 | .76 | .69 | 1.3 | 1.4 | 1.3 | 1.4 | 1.1 |
| 54 | 2.6 | 40 | 5 | 40 | 6 | 41 | 4 | .35 | .35 | 0.37 | 0.37 | ..... | 0.38 | 0.36 |
| 56 | 2.9 | 37 | 11 | 37 | 12 | 37 | 8 | .24 | .25 | ..... | .32 | ..... | .34 | .29 |
| 57 | 2.9 | 39 | 6 | 39 | 12 | 39 | 7 | .37 | .38 | .37 | .36 | .35 | .38 | .37 |
| 59 | 3.0 | 39 | 6 | 39 | 9 | 39 | 7 | .34 | .35 | ..... | .37 | .36 | .37 | .36 |
| 61 | 3.2 | 37 | 13 | 37 | 8 | 38 | 10 | .30 | .29 | .31 | .31 | .33 | .33 | .31 |
| 65 | 4.0 | 39 | 7 | 40 | 9 | 39 | 6 | .29 | .30 | .32 | .31 | .32 | .33 | .31 |
| 67 | 5.2 | 39 | 9 | 40 | 13 | 43 | 27 | 1.8 | 1.9 | 2.9 | 2.9 | ..... | 3.7 | 2.6 |
| 68 | 6.6 | 41 | 6 | 41 | 7 | 40 | 6 | 1.9 | 1.9 | 2.5 | 2.7 | ..... | 2.8 | 2.4 |
| 72 | 7.7 | 38 | 4 | 38 | 8 | 39 | 9 | 2.7 | 2.6 | 3.8 | 3.5 | 3.7 | 3.7 | 3.3 |
| 73 | 9.0 | 36 | ..... | 37 | 8 | 38 | 11 | 6.0 | 6.3 | 5.0 | 5.0 | 5.5 | 5.7 | 5.6 |
| 74 | 11.6 | 32 | 7 | 35 | 30 | 32 | 8 | 2.3 | 2.3 | 3.2 | 2.8 | 3.1 | 2.8 | 2.8 |
| 75 | 11.7 | 37 | 9 | 38 | 13 | 37 | 11 | 2.9 | 2.8 | 3.9 | 3.5 | 3.1 | 3.1 | 3.2 |
| **SERIES D—MAGNESIAN HYDRATED LIMES** | | | | | | | | | | | | | | |
| 77 | 5.9 | 43 | 6 | 42 | 5 | 43 | 6 | 0.43 | 0.42 | ..... | 0.54 | 0.57 | 0.53 | 0.50 |
| 78 | 7.2 | 41 | 9 | 41 | 8 | 41 | 13 | .35 | .36 | 0.40 | .40 | .41 | .39 | .39 |
| 80 | 12.7 | 41 | 6 | 38 | 4 | 40 | 7 | .64 | .65 | .69 | .68 | .75 | .76 | .70 |

TABLE 5. *Effect of varying the cement on the expansion of cement-lime bars prepared in the proportion of 1 cement:1 lime (by weight), and autoclaved at a steam-gage pressure of 295 lb/in.² for 3 hr*

[The expansions of the 17 cements without the addition of limes ranged from 0.0 to 0.30 percent and are shown in brackets. The percentage of expansion obtained after subtracting the percentage of expansion of the cement from the percentage of expansion of the cement-lime bar is given in parentheses.]

| Lime number | Unhydrated oxides | Linear expansion of cement-lime bars prepared with cements 1 to 17, inclusive | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 [0.00] | 2 [0.01] | 3 [0.01] | 4 [0.02] | 5 [0.04] | 6 [0.04] | 7 [0.06] | 8 [0.07] | 9 [0.11] | 10 [0.11] | 11 [0.11] | 12 [0.17] | 13 [0.18] | 14 [0.19] | 15 [0.23] | 16 [0.27] | 17 [0.30] |
| **SERIES A—HIGH-CALCIUM HYDRATED LIMES** | | | | | | | | | | | | | | | | | | |
| | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % |
| 1 | 0.0 | --- | --- | --- | --- | --- | --- | --- | 0.11<br>(.04) | --- | 0.19<br>(.08) | --- | --- | 0.43<br>(.25) | --- | --- | 0.44<br>(.17) | --- |
| 2 | .0 | --- | --- | --- | --- | --- | 0.07<br>(.03) | --- | --- | 0.13<br>(.02) | 0.20<br>(.09) | --- | --- | --- | --- | 0.26<br>(.03) | --- | --- |
| 3 | .0 | --- | --- | --- | --- | --- | --- | --- | --- | --- | 0.16<br>(.05) | --- | --- | 0.39<br>(.21) | --- | --- | 0.39<br>(.12) | --- |
| 4 | .0 | 0.03<br>(.03) | --- | --- | 0.05<br>(.03) | --- | --- | 0.08<br>(.02) | --- | --- | 0.15<br>(.04) | --- | --- | --- | --- | --- | --- | 0.29<br>(−.01) |
| 5 | .0 | --- | --- | --- | --- | --- | 0.07<br>(.03) | --- | --- | --- | 0.13<br>(.02) | --- | --- | 0.31<br>(.13) | 0.15<br>(−.04) | 0.29<br>(.06) | 0.30<br>(.03) | --- |
| 6 | .0 | 0.05<br>(.05) | --- | --- | --- | --- | --- | 0.11<br>(.05) | --- | --- | 0.19<br>(.08) | --- | --- | --- | --- | --- | --- | 0.39<br>(.09) |
| 12 | 1.1 | --- | --- | --- | --- | --- | 0.07<br>(.03) | --- | --- | 0.13<br>(.02) | 0.19<br>(.08) | --- | --- | --- | --- | --- | 0.62<br>(.35) | --- |
| 13 | 1.1 | --- | 0.09<br>(.08) | --- | --- | --- | 0.10<br>(.06) | --- | --- | --- | 0.20<br>(.09) | --- | --- | --- | --- | --- | 0.47<br>(.20) | --- |
| 14 | 1.2 | --- | --- | --- | --- | --- | 0.09<br>(.05) | --- | --- | 0.14<br>(.03) | 0.19<br>(.08) | --- | --- | --- | --- | --- | 0.36<br>(.09) | --- |
| 15 | 1.6 | --- | --- | --- | --- | --- | --- | --- | 0.10<br>(.03) | --- | 0.18<br>(.07) | --- | --- | --- | 0.17<br>(−.02) | 0.32<br>(.09) | 0.37<br>(.10) | --- |
| 19 | 2.3 | --- | --- | --- | --- | --- | 0.11<br>(.07) | --- | --- | --- | 0.24<br>(.13) | --- | --- | 0.48<br>(.30) | 0.24<br>(.05) | 0.32<br>(.09) | 0.72<br>(.45) | --- |
| **SERIES B—REGULARLY HYDRATED DOLOMITIC LIMES** | | | | | | | | | | | | | | | | | | |
| 22 | 16.1 | 6.8<br>(6.8) | --- | --- | --- | --- | --- | 8.0<br>(7.9) | --- | --- | 8.8<br>(8.7) | --- | --- | --- | --- | --- | --- | 9.4<br>(9.1) |
| 32 | 26.8 | --- | 13.0<br>(13.0) | --- | --- | --- | --- | 10.6<br>(10.5) | --- | --- | 12.0<br>(11.9) | --- | --- | --- | --- | --- | --- | 11.9<br>(11.6) |
| 35 | 27.7 | --- | 15.1<br>(15.1) | --- | --- | --- | --- | 16.3<br>(16.2) | --- | --- | 16.5<br>(16.4) | --- | --- | --- | --- | --- | --- | 16.4<br>(16.1) |
| 37 | 29.3 | --- | 5.7<br>(5.7) | --- | 5.9<br>(5.9) | 7.6<br>(7.6) | --- | --- | --- | --- | 7.3<br>(7.2) | 7.1<br>(7.0) | --- | --- | --- | --- | --- | --- |

TABLE 5. *Effect of varying the cement on the expansion of cement-lime bars prepared in the proportion of 1 cement:1 lime (by weight), and autoclaved at a steam-gage pressure of 295 lb/in.² for 3 hr*—Continued

[The expansions of the 17 cements without the addition of limes ranged from 0.0 to 0.30 percent and are shown in brackets. The percentage of expansion obtained after subtracting the percentage of expansion of the cement from the percentage of expansion of the cement-lime bar is given in parenthesis]

| Lime number | Unhydrated oxides | Linear expansion of cement-lime bars prepared with cements 1 to 17, inclusive | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 [0.00] | 2 [0.01] | 3 [0.01] | 4 [0.02] | 5 [0.04] | 6 [0.04] | 7 [0.06] | 8 [0.07] | 9 [0.11] | 10 [0.11] | 11 [0.11] | 12 [0.17] | 13 [0.18] | 14 [0.19] | 15 [0.23] | 16 [0.27] | 17 [0.30] |
| **SERIES C—HIGHLY HYDRATED DOLOMITIC LIMES** | | | | | | | | | | | | | | | | | | |
| | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % |
| 49 | 1.4 | ... | ... | ... | ... | ... | ... | ..... | ... | ... | 0.25<br>(.14) | ... | ... | ... | ... | ... | 0.51<br>(.24) | ..... |
| 53 | 2.6 | ... | 0.21<br>(.21) | ... | 0.31<br>(.29) | ... | ... | 0.42<br>(.36) | ... | ... | 1.4<br>(1.3) | ... | 2.9<br>(2.7) | 1.6<br>(1.4) | ... | ... | ..... | 2.7<br>(2.4) |
| 54 | 2.6 | ... | ... | ... | | ... | 0.21<br>(.17) | ... | ... | ... | 0.37<br>(.26) | ... | ... | 0.57<br>(.39) | 0.40<br>(.21) | 0.46<br>(.23) | 0.69<br>(.42) | ..... | ..... |
| 56 | 2.9 | ... | ... | ... | ... | ... | ... | ... | 0.30<br>(.13) | ... | 0.33<br>(.22) | ... | ... | 0.85<br>(.67) | ... | 0.40<br>(.17) | ..... | ..... |
| 57 | 2.9 | 0.25<br>(.25) | ... | ... | ... | ... | ... | 0.23<br>(.17) | ... | ... | 0.37<br>(.26) | ... | ... | ... | ... | ... | ..... | 0.57<br>(.27) |
| 59 | 3.0 | ... | ... | ... | ... | ... | 0.22<br>(.18) | ... | ... | 0.26<br>(.15) | 0.37<br>(.26) | ... | ... | ... | ... | ... | 0.62<br>(.35) | ..... |
| 60 | 3.2 | ... | ... | 0.22<br>(0.21) | ... | 0.21<br>(.17) | ... | ... | ... | ... | 0.36<br>(.25) | ... | ... | ... | ... | ... | 0.73<br>(.46) | ..... |
| 61 | 3.2 | ... | 0.19<br>(.18) | ... | ... | ... | ... | 0.19<br>(.13) | ... | ... | 0.32<br>(.21) | ... | ... | ... | ... | ... | ..... | 0.47<br>(.17) |
| 65 | 4.0 | ... | ... | ... | 0.16<br>(.14) | ... | ... | ... | ... | ... | 0.32<br>(.21) | ... | ... | ... | 0.32<br>(.13) | 0.36<br>(.13) | 0.51<br>(.24) | ..... |
| 67 | 5.2 | 1.8<br>(1.8) | 0.45<br>(.44) | 2.4<br>(2.4) | ... | 1.8<br>(1.8) | ... | 1.3<br>(1.2) | ... | ... | 3.2<br>(3.1) | 2.3<br>(2.2) | 2.6<br>(2.5) | ... | ... | ... | ..... | 2.9<br>(2.6) |
| 73 | 9.0 | ... | 1.9<br>(1.9) | 4.7<br>(4.6) | ... | ... | ... | ... | ... | ... | 5.3<br>(5.2) | ... | 5.5<br>(5.3) | ... | ... | ... | ..... | 6.1<br>(5.8) |
| 74 | 11.6 | ... | 0.69<br>(.68) | ... | ... | ... | ... | ... | ... | ... | 3.0<br>(2.9) | ... | 3.5<br>(3.3) | ... | ... | ... | ..... | 4.1<br>(3.8) |
| **SERIES D—MAGNESIAN HYDRATED LIMES** | | | | | | | | | | | | | | | | | | |
| 77 | 5.9 | ... | ... | ... | 0.21<br>(.19) | ... | ... | ... | ... | 0.33<br>(.22) | 0.55<br>(.44) | ... | ... | ... | ... | 0.95<br>(.72) | ... | ..... |
| 78 | 7.2 | 0.26<br>(.26) | 0.26<br>(.25) | ... | 0.24<br>(.22) | ... | ... | 0.31<br>(.25) | ... | ... | 0.40<br>(.29) | ... | 0.44<br>(.27) | ... | ... | ... | ... | 0.58<br>(.28) |
| 80 | 12.7 | 0.54<br>(.54) | ... | ... | 0.42<br>(.40) | ... | ... | 0.53<br>(.47) | ... | ... | 0.69<br>(.58) | ... | ... | 0.68<br>(.50) | ... | ... | ... | 0.90<br>(.60) |

standard method of test for autoclave expansion of portland cement [6]) are given in brackets directly below the numerical listings of the cements. The values for the percentage of expansion of the cement-lime bars are listed in each column. In addition, the percentage of expansion obtained after subtracting the percentage of expansion of the cements from the percentage of expansion of the cement-lime bars is given in parentheses.

The data are insufficient for the application of statistical analysis. Nevertheless, several pertinent observations may be made. Inspection of the expansion values of the cement-lime bars of a particular lime reveals that as the expansion value of the constituent cements increases there is a definite trend for the expansion value of the cement-lime bars to increase also. This indicates that the expansion of the cement used is a factor of moment, and that it is necessary to apply a correction for the expansion contributed by the cement. By the method of trial and error, it can be shown that arbitrarily subtracting the expansion of the neat cement from the total expansion of the cement-lime bar gives the most uniform results for the "net" expansion of a lime. Net expansion values obtained in this manner are shown in parentheses in table 5. Even the net expansion values for a particular lime, however, tend to increase somewhat as the expansion values of the cements increase. For purposes of a test procedure, the variation in net expansion values could be further reduced by eliminating the use of cements of very low or high expansion. For example, good agreement of net expansion values is shown in most instances when the expansion values of the neat cements range between 0.05 and 0.15 percent.

It is realized that the above conclusions are based on limited data and that it would have been desirable to have determined the expansion values of all the limes with all the cements. Unfortunately, this phase of the investigation was the last undertaken, and a more complete study was no longer possible because of the limited quantity of materials remaining.

## 5. Behavior of Cement-Lime Specimens During Course of Autoclaving [7]

### (a) Expansion of Specimens During Normal Heating Schedule of Special Autoclave

Figure 12 shows the normal heating schedule of the specially equipped autoclave; the thermal expansion of the parts of the autoclave, including the thermal expansion of the bar; and the expansion of bars prepared with three regularly hydrated dolomitic limes, three highly hydrated dolomitic limes, and one neat portland cement. The thermal expansion reached 0.4 percent at 216° C (steam-gage pressure of 295 lb/in.$^2$). Subtracting this value from that recorded for portland cement at 216° C, or 0.6 percent, gives the value of 0.2 percent for the expansion of the neat portland-cement bar as compared with 0.11 as determined in accordance with the standard method of test for autoclave expansion of portland cement. It is believed that this slight difference in determining percentage of expansion of the cement can in part be ascribed to the method used in determining the percentage of thermal expansion. However, inasmuch as the thermal expansion is insignificant when compared to the expansions of bars prepared with hydrated limes containing appreciable quantities of unhydrated oxide, no further studies were made to determine whether the thermal expansion could be ascertained more accurately.

The curves representing the expansion of the neat portland-cement bar and the cement-lime bars shown in figure 12 involve not only the thermal expansion but also the expansion accompanying the hydration of the constituents of the test specimens. To obtain the expansion other than thermal, one should therefore subtract the percentage of thermal expansion at any specified time from the total percentage of expansion as shown in figure 12.

The seven curves depicting the expansion characteristics of the cement-lime bars shown in figure 12 were chosen primarily because they were mor

[7] The authors are indebted to G. J. Fink and Emil Trattner for the use their data on the behavior of cement-lime specimens during the course autoclaving, previously presented at the Twenty-Eighth Annual Convent of the National Lime Association, March 1946.

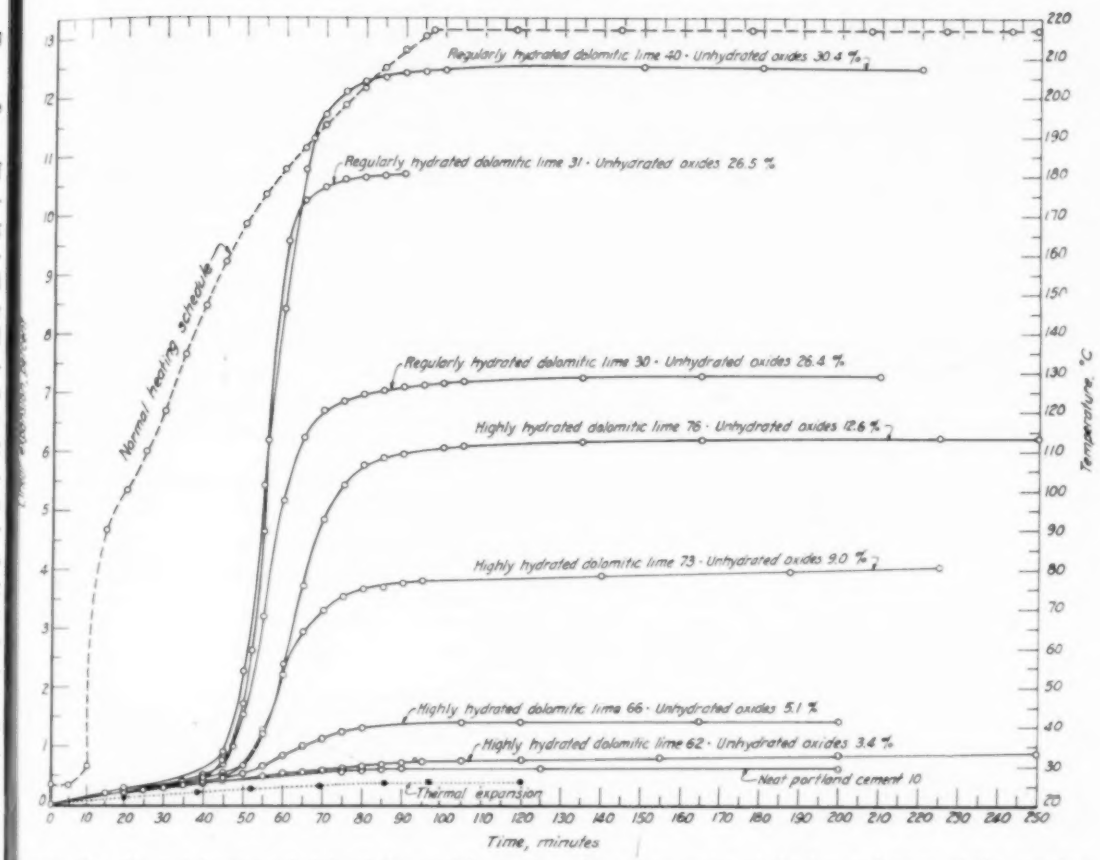
Regularly hydrated dolomitic lime 40 · Unhydrated oxides 30.4 %
Regularly hydrated dolomitic lime 31 · Unhydrated oxides 26.5 %
Normal heating schedule
Regularly hydrated dolomitic lime 30 · Unhydrated oxides 26.4 %
Highly hydrated dolomitic lime 76 · Unhydrated oxides 12.6 %
Highly hydrated dolomitic lime 73 · Unhydrated oxides 9.0 %
Highly hydrated dolomitic lime 66 · Unhydrated oxides 5.1 %
Highly hydrated dolomitic lime 62 · Unhydrated oxides 3.4 %
Neat portland cement 10
Thermal expansion
Time, minutes
Temperature, °C

FIGURE 12. *Normal heating schedule of the special autoclave, thermal expansion of the bar and parts of the autoclave, expansion of a neat portland cement bar, and expansions of cement-lime bars prepared with three regularly hydrated and three highly hydrated dolomitic limes in the proportion of 1C:1L.*

or less typical of those obtained with other hydrated limes over this range of expansion. No curve showing the expansion of a cement-lime bar prepared with a high-calcium lime is plotted in figure 12, since such a curve would be obscured because it would very closely coincide with the one plotted for the portland cement. It can be seen from figure 12 that the curves expressing the expansion of the cement-lime test specimens are S-shaped, with a flattening accompanying a decrease in the total expansion. At the normal heating schedule, only a slight amount of the total expansion occurred before the elapse of 45 min, or before a temperature of about 150° C was reached. This was followed by a rapid rate of expansion which, in turn, tapered off before a temperature of 216° C was reached. Consequently, there is little to be gained by continuing the heating at 216° C for more than 1 hr.

After subtracting the percentage of expansion of the parts of the autoclave at 216° C from each of the values of the cement-lime bars at the same temperature and comparing the percentages of expansion thus obtained with those recorded in table 1 for similar 1:1 cement-lime bars, it was found that the expansions obtained with the special autoclave were for the most part appreciably lower than those recorded in table 1. The most logical explanation for the lower percentage of expansion with the use of the special autoclave appeared to be associated with the lower rate of temperature rise during autoclaving. Consequently, a series of experiments was made of the

rate of expansion of the cement-lime specimens when heated in the special autoclave at a still further retarded rate.

**(b) Effect of Retarding Rate of Heating on Expansion**

The results obtained with three of the limes (40, 73, and 66) are plotted in figure 13. The retardation was started at the end of 30 min, or when the temperature reached 120° C. At this point, but little expansion had occurred in the specimens. The rate of heating was then retarded so that the temperature did not reach 216° C until the end of 175 min, rather than 97 min as in the case of the normal rate of heating. From figure 13 it is evident that not only was the rate of expansion retarded at the slower rate of heating, but, more important, the total expansion was decidedly less. These experiments show the great importance of defining the heating schedule of an autoclave, by a specification for the autoclave testing of expansion of a cement-lime specimen.

## VII. Application of Results to Selection of a Proposed Specification for Soundness of Hydrated Lime

It should be recalled that the primary purpose of the investigation was to study the expansive characteristics of hydrated limes and to obtain data and information that might be used in formulating an accelerated performance test acceptable for a specification for the soundness of hydrated limes.

Accelerated performance tests have been incorpo-

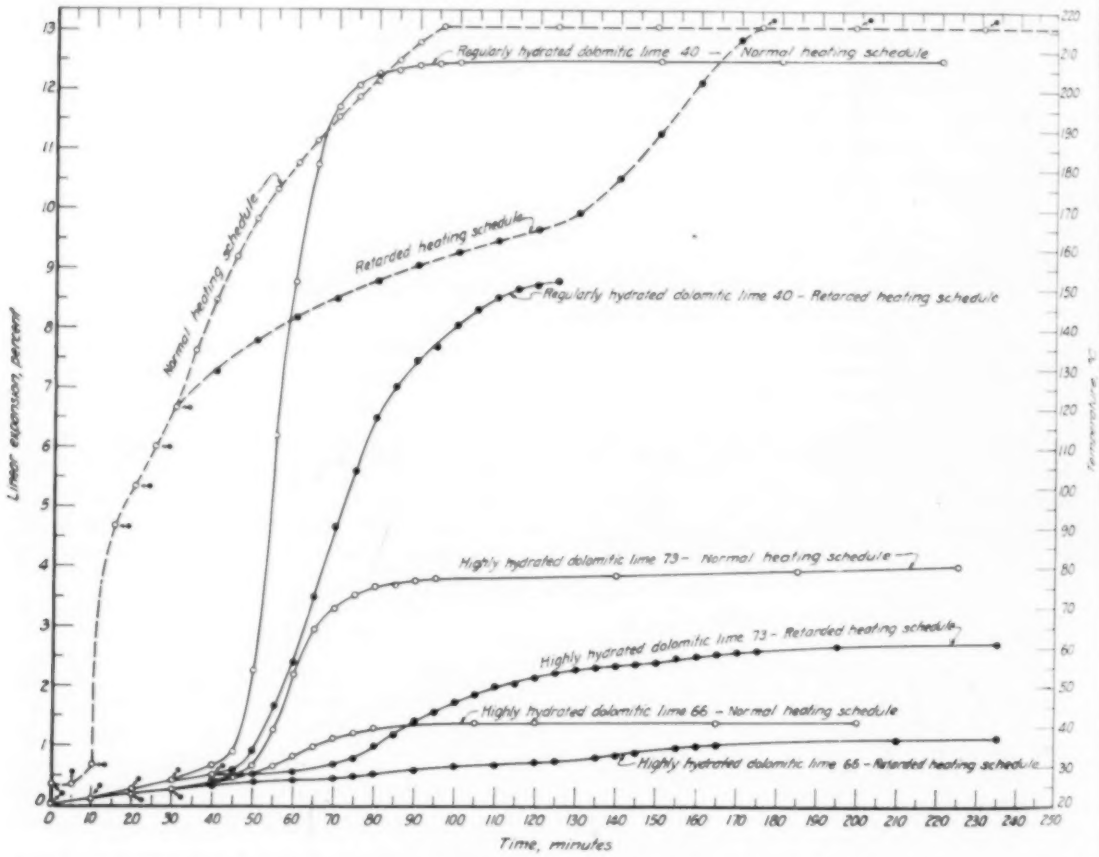
Regularly hydrated dolomitic lime 40 — Normal heating schedule
Normal heating schedule
Retarded heating schedule
Regularly hydrated dolomitic lime 40 - Retarded heating schedule
Highly hydrated dolomitic lime 73 - Normal heating schedule
Highly hydrated dolomitic lime 73 - Retarded heating schedule
Highly hydrated dolomitic lime 66 - Normal heating schedule
Highly hydrated dolomitic lime 66 - Retarded heating schedule
Linear expansion, percent
Time, minutes

FIGURE 13. *Effect of decreasing the rate of heating the special autoclave to 216° C (equivalent to gage-pressure of 295 lb/in.²) on the rate of expansion and total expansion of cement-lime bars prepared with three hydrated limes.*

rated into many specifications for the selection of various materials. The need of a test that both accelerates and amplifies the potential expansion of a hydrated lime in service is apparent from considerations of a typical plaster failure involving expansion. Figure 14 shows a marked failure that occurred in white coat along the side of a concrete beam when the expansion of this coat became excessive. Chemical and thermal analyses indicated that the white coat had been prepared from a mixture of gypsum gaging plaster and a normally hydrated dolomitic finishing lime that had contained considerable unhydrated MgO. The slow hydration of the MgO in the set and hardened white coat to $Mg(OH)_2$ had resulted in a cumulative expansion of such a magnitude that the white coat had sheared away from the underlying base coat of gypsum bond plaster that had been applied to the concrete beam. Calculations based on measurements of the bulge in the white coat revealed that a linear expansion as low as 0.5 percent appears to account for a separation of the magnitude shown in figure 14. The fact that such

FIGURE 14. *Plaster failure involving the expansion of about 0.5 percent in the white coat along the side of a concrete beam.*

failures usually do not take place until some 5 to 10 yr (or longer) after a building has been erected shows the necessity of an accelerated test for judging the soundness of hydrated lime, provided a performance test is to be used. Also, the fact that only a very small expansion can be tolerated within a set and hardened plaster or mortar without causing trouble shows the desirability of amplification of the potential expansion of the constituents composing the plaster or mortar. There is no valid reason for not accepting an accelerated test procedure that amplifies expansion provided it clearly differentiates hydrated limes having low potential expansions from all others. In fact, amplification has a definite advantage in that it facilitates this differentiation.

The factors to be considered in the selection of a method best suited for an accelerated performance test, and the selection of a plausible limit to the percentage of expansion will now be discussed. However, it is not the purpose at this time to write a detailed specification.

### 1. Selection of Method

The selection of a test procedure for a specification for soundness of hydrated lime should be based on several criteria. Among the most important of these are the following:

1. The test should clearly differentiate the hydrated limes having low potential expansions from all others.
2. The procedure should be reproducible.
3. It should not be necessary to repeat the test too often because of such factors as frequent breakage of weak test specimens in handling.
4. The time required to complete the test should be as short as feasible.
5. The procedure, if possible, should be adaptable to apparatus already available in numerous testing laboratories.

On the basis of these criteria, autoclave testing at a steam-gage pressure of 25 lb/in.$^2$ would be eliminated by criterion 4, because at this pressure ultimate expansion of cement-lime bars is not attained even after 7 hr of autoclaving (fig. 5). On the other hand, the time period required for autoclaving at 295 lb/in.$^2$ is much shorter, actually slightly over 3 hr, for the entire procedure of autoclaving, divided as follows: Time of raising pressure to 295 lb/in.$^2$, from 1 to 1¼ hr; time of continued heating at this pressure, 1 hr (see fig. 12); and time of cooling autoclave, 1 hr. Furthermore, autoclaving at 295 lb/in.$^2$ seems particularly desirable, because numerous testing and research laboratories throughout the country are equipped with autoclaves so designed that the gage pressure can be raised to 295 lb/in.$^2$ within 1 to 1¼ hr and automatically maintained thereafter at this pressure. Autoclaving at 295 lb/in.$^2$, therefore, meets both criteria 4 and 5.

Although a test procedure very likely could be devised for autoclaving cement-lime specimens at some gage pressure between 25 and 295 lb/in.$^2$, it is doubtful if autoclaving at an intermediate pressure would have any advantages over autoclaving at 295 lb/in.$^2$.

The next factor to be discussed is the selection of that ratio of cement to lime in the test specimen that gives the best indication of the potential expansion of hydrated limes. All three ratios (2C:1L, 1C:1L, and 1C:2L) could be used to differentiate the regularly hydrated dolomitic limes, characterized by having the highest percentages of unhydrated oxides and the highest percentages of expansion, from the remaining hydrated limes (figs. 7, 8, and 9). There are, however, certain of the highly hydrated dolomitic limes that apparently have appreciable potential expansions when tested in the proportions of 1C:1L or 1C:2L that do not clearly show this expansive potentiality when tested in the proportion of 2C:1L (fig. 10). With a 2C:1L proportion, the percentages of expansion of all the highly hydrated dolomitic limes are distributed rather uniformly over a narrow range—with but one exception, from 0.18 to 0.88 percent. Therefore, a 2C:1L proportion does not meet criterion 1.

In the 1C:1L and 1C:2L proportions, the highly hydrated dolomitic limes of low potential expansions are easily differentiated from those of appreciable potential expansion. But, as mentioned previously, 1C:2L bars are fragile and difficult to handle without excessive breakage. Therefore, by criterion 3, testing hydrated limes in the 1C:2L proportion is eliminated. Consequently, having eliminated the 2C:1L and 1C:2L proportions, the 1C:1L proportion remains the most desirable. Since it has been shown that the procedure of testing the cement-lime bars in the 1C:1L proportion is reproducible, criterion 2 is also met. In conclusion, therefore, testing cement-lime bars prepared in the proportion of 1C:1L and autoclaving at 295 lb/in.$^2$ meets all of the criteria set forth for a procedure for determining the soundness of hydrated limes.

### 2. Proposed Limit of Percentage of Expansion

Bearing in mind that the test for soundness should differentiate hydrated limes having low potential expansions from all others, and that "Not a single instance has been found where bulging occurred in a white-coat plaster made with high-calcium lime;" [2], it would appear logical to limit the percentage of expansion to that shown by the high-calcium limes. If the upper limit is placed at 0.6 percent without subtracting the percentage of expansion of the cement, then all of the high-calcium limes would be included and 16 of the highly hydrated dolomitic limes; but at the same time those highly hydrated dolomitic limes that showed moderately high potential expansion would be eliminated. The limit of 0.6 percent may be too restrictive in view of the fact that certain cements might be used that give slightly higher expansion than cement 10, which was used in the bulk of the experiments in the present investigation. It is proposed, therefore, that the upper limit of the linear expansion for a test for soundness be placed at 1.0 percent after subtracting the percentage of expansion of the cement.

It is further proposed that portland cement meeting the requirements of Federal Specification SS–C–192 (type I) for portland cement (ASTM Designation: C 150–46) be used in preparing the 1C:1L test bars, and in addition that only those cements having expansions ranging from 0.05 to 0.15 be selected.

A limit of 1.0 percent should afford adequate protection for the consumer and not work an undue hardship on the producer. All high-calcium hydrated limes and quicklimes, if properly slaked so that the unhydrated oxide is reduced to a low percentage, will easily meet the requirement; and apparently if the highly hydrated dolomitic limes have been hydrated to the extent that the unhydrated oxide is reduced to less than 5 percent, such products should also meet the requirement. The 16 highly hydrated dolomitic limes that meet this requirement were all commercially produced. The remaining 12 do not represent a true cross-section of this type of lime as now being produced. Six, as stated previously, were experimental limes, and the process of manufacture of several of the others has been modified, so that there is good reason to believe that the percentages of unhydrated oxide and the expansions are now of the order of magnitude of the high-calcium limes.

All of the four magnesian limes with the percentage of unhydrated oxide ranging from 5.9 to 12.7 would meet the 1-percent limit on expansion. Two of these, namely, limes 79 and 80, with 9.8 and 12.7 percent of unhydrated oxide, respectively,

would not, however, meet a composition requirement that the quantity of unhydrated oxide shall not exceed 8 percent by weight on the as-received basis [3, 4].

On the other hand, it is obvious that certain of the highly hydrated dolomitic limes having quantities of unhydrated oxide as low as 8 percent can, nevertheless, exhibit appreciable autoclave expansion. In either case, since an accelerated performance test should be preferable to a limitation of the chemical composition, it is believed that a limit of 1 percent on the expansion of 1C:1L bars is better than the 8-percent limit on the unhydrated oxides.

## VIII. Summary

An investigation of the expansive characteristics of hydrated limes was completed, and from the data obtained an accelerated performance test was proposed for testing the soundness of hydrated lime.

Samples of 80 structural hydrated limes, representative of the production in the United States, were classified on the basis of chemical analyses and calculated unhydrated oxide content as high-calcium, regularly hydrated dolomitic, highly hydrated dolomitic, and magnesian limes. The percentage of unhydrated oxide for the high-calcium class ranged from 0 to 3.9; for the regularly hydrated dolomitic from 16.1 to 34.3; for the highly hydrated dolomitic from 1.4 to 12.6; and for the magnesian from 5.9 to 12.7.

On the basis of preliminary experiments, portland cement was selected as the most suitable hydraulic material for gaging hydrated lime in the preparation of test specimens suitable for autoclaving. A technique for preparing, curing, and autoclaving 1- by 1- by 10-in. cement-lime bars was developed. The method for determining the linear expansion of cement-lime bars prepared in the proportion of 1 cement to 1 lime, by weight, and subsequently autoclaved at 295 lb/in.$^2$ for 3 hr was found to be reproducible by three independent operators.

Data on the expansions of cement-lime bars prepared in proportions of 2 parts cement to 1 part lime, 1 part cement to 1 part lime, and 1 part cement to 2 parts lime, by weight, and autoclaved to 295 lb/in.$^2$ gage pressure for 3 hr, showed that bars prepared with the regularly hydrated dolomitic limes, which had the highest percentages of unhydrated oxide, had the highest percentage of expansion. The high-calcium limes, characterized, in general, by the lowest percentages of unhydrated oxide, gave the lowest percentage of expansion. Most of the highly hydrated dolomitic limes had percentages of unhydrated oxide and expansions that were comparable to those of the high-calcium limes. The remainder had percentages of unhydrated oxide and expansions that were greater than those of the high-calcium limes. The four magnesian limes exhibited unique behavior in that each showed lower percentage of expansion than other limes with comparable percentages of unhydrated oxide.

An increase in the proportion of lime in the cement-lime bars was attended by an increase in expansion and by better differentiation between the classes within a series. Bars of the 1 part cement to 2 parts lime series, however, were very weak and were eliminated from consideration for a routine test method.

The effect of 17 different portland cements on the expansion of cement-lime (1:1 by weight) bars was investigated. The neat cements ranged in expansion from 0.00 to 0.30 percent, and they were tested in part with 30 selected limes. The expansion values of cement-lime bars for a particular lime tended to increase as the expansion value of the constituent cement increased. Arbitrarily subtracting the expansion of the neat cement from the total expansion of the cement-lime bar gave the most uniform results for the net expansion of the lime.

An autoclave was specially modified for ascertaining the behavior of cement-lime specimens during the course of autoclaving. The results showed that only a slight amount of the total expansion of cement-lime bars occurred before a temperature of 150° C was reached. Above 150° C, a rapid expansion rate was noted, which, in turn, tapered off before a temperature of 216° C was reached. Since little expansion occurred after the specimen had reached the limiting temperature of 216° C (equivalent to 295 lb/in.$^2$, steam-gage pressure), it was concluded that continued heating at 216° C beyond 1 hr is unnecessary for a test procedure. The results also indicated the importance of a controlled rate of heating the autoclave to 216° C, as a decreased rate of heating gave decreased expansions.

It was proposed that hydrated limes be tested

n the proportion of 1 cement:1 lime (by weight), that the cement used have an expansion between 0.05 and 0.15 percent, that the autoclaving be done at 295 lb/in.$^2$ gage pressure for 1 hr according to a controlled schedule and, finally, that the expansion obtained after subtracting the percentage of expansion of the neat cement bar from the total expansion of the cement-lime bar be limited to not more than 1 percent.

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The authors express thanks and appreciation to Emil Trattner and G. J. Fink, former Research Associates at the National Bureau of Standards, for obtaining a great portion of the data on autoclave tests included in this publication.

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# Concentration of Isotopes of Mercury in Countercurrent Molecular Stills [1] [2]

By Samuel L. Madorsky, Paul Bradt, and Sidney Straus

Mercury was refluxed in countercurrent molecular stills in order to concentrate $^{204}Hg$. Two glass stills, with heater and cooler placed outside the distillation columns, and one still, consisting of a glass column heated externally and a stainless-steel cooler placed concentrically inside the column, were used. As compared with a 10-cell steel column described previously, these columns showed poor performance, mainly because the hold-up was too small. There are definite indications, however, that with liquids having a lower surface tension than Hg, these columns will perform as well as the 10-cell steel column. Mass-spectrometer analyses of isotope ratios of the Hg-isotope concentrates were in good agreement with density determinations.

## I. Introduction

In a previous paper [1] [3] concentration of the isotopes of mercury in a countercurrent molecular still has been described. The still consisted of a 10-cell metal column inclosed in a glass cylinder. The end fractions differed in density by a total of 161.6 ppm. The maximum change of density obtained per cell was about 18 ppm as compared with a maximum value of about 24 ppm obtained in a single-stage small glass still [2] or 23 ppm obtained in a single-stage large steel apparatus [3]. One object of this investigation was to explore the possibility of obtaining by the same method a large separation of the isotopes of mercury by using long distillation columns with many cells. Another object was to compare density measurements of mercury-isotope concentrates with mass-spectrometer analysis of isotope ratios in the same concentrates.

Ordinary mercury consists of a mixture of seven stable isotopes in the following proportions [4]:

| Isotope | Mole % |
|---|---|
| 196 | 0.15 |
| 198 | 10.1 |
| 199 | 17.0 |
| 200 | 23.3 |
| 201 | 13.2 |
| 202 | 29.6 |
| 204 | 6.7 |

There has been of late a great deal of interest in the possibility of using pure isotopes of Hg of even atomic weight as a primary standard of wavelength of light [5]. Although $^{200}Hg$ and $^{202}Hg$ are the most abundant isotopes, it would be very difficult to separate them or even to concentrate them by countercurrent molecular distillation as this method is adapted primarily to the concentration of either the lightest or heaviest isotope from a mixture. The same argument holds for $^{198}Hg$. As to a choice between $^{196}Hg$ and $^{204}Hg$, it is obvious from the abundance table that $^{204}Hg$ is

[1] The work described in this paper was done in part under the auspices of the Atomic Energy Project.

[2] The molecular stills used in concentrating mercury isotopes are similar in design to those developed in this laboratory by S. L. Madorsky, A. K. Brewer, and T. I. Taylor.

[3] Figures in brackets indicate the literature references at the end of this paper.

preferable because it is about 45 times as abundant as $^{198}$Hg. In view of these considerations, the main object of this investigation was the concentration of the heavy isotopes, particularly $^{204}$Hg.

## II. Distillation Columns

The distillation columns used in this work are of two types: I, consisting of a glass tube, with heater and cooler placed outside the tube, figure 1; and II, consisting also of a glass tube and with heater placed outside, but with the cooler placed inside the tube, figure 2. Both columns were kept at an angle of 7.5° to the horizontal. They were provided with reservoirs at their upper ends so that only heavy fractions were concentrated at the lower ends. Inlets at the ends served for the introduction of the mercury and for drawing samples for analysis. The reservoirs were provided with side branch tubes surrounded with nichrome heating coils for the circulation of the mercury in the reservoirs. Evacuation was accomplished by means of an oil pump and Hg-vapor pump, and a pressure of about $10^{-6}$] mm of Hg was maintained during the operation of the stills.

Column I, figure 1, was made of a glass tube with an internal diameter of 21 mm. Indentations pressed into the tube on the underside, at right angles to the axis of the tube, formed individual cells, or cups. Roofs over these cups were formed on the upper side of the tube by indenting the glass in such a way that the condensate over each cup was delivered to the cup immediately above it in the series. Condensate on the sides of the column was guided from cell to cell in the upward direction by means of gutters pressed into the glass column. The column rested on a Nichrome electric heater. The roofs were cooled by means of a stream of tap water flowing over them in a trough. This trough was made by pressing lucite plates against the sides of the distillation column, with strips of sponge rubber between the lucite and the glass to make the joints watertight.

Column II, figure 2, was made of a glass tube 48 mm in inside diameter. The cups, or cells, were shaped in the same way as in column I. The condenser consisted of a series of metal plate-roofs strung on a metal tube with tight-fitting sleeves as spacers. The metal tube was water-cooled through a smaller concentric metal tube. The metal parts exposed to mercury were made of stainless steel. The column rested on a Nichrome electric heater. The sides and top were covered with an asbestos mat 2 cm thick in order to keep the column hot and to prevent the mercury vapor from condensing on the inner surface.

In addition to these two columns, a third column, III, similar to column I, but without a reservoir, was used in this work. In the absence of a reservoir a light concentrate could be collected at the upper end in addition to the heavy concentrate at the lower end. The cooler for this column, instead of a direct stream of water over the roofs, consisted of several long water-cooled copper tubes connected to two manifolds at the ends and placed over the column roofs. Contact between this cooler and the roofs was made by means of granular magnetic-iron oxide. The column was placed at an angle of 3.75° to the horizontal. Characteristic details of the three distillation columns are given in table 1.

TABLE 1. *Details of molecular distillation columns used in concentrating isotopes of mercury*

| Column | Number of cells | Hg in each cell | Angle to horizontal |
|---|---|---|---|
| | | *g* | *Degrees* |
| I. All glass with reservoir | 66 | 8 | 7.50 |
| II. Glass jacket reservoir, and internal metal cooler | 110 | 12 | 7.50 |
| III. All glass, without reservoir | 150 | 8 | 3.75 |

## III. Temperature Measurements and Density Determinations of Fractions

Operation of the columns could be observed and kept under control through a series of thermocouples placed on the outside of the columns at various points between them and the heaters. However, as pointed out in a previous paper [1], temperature measurements taken outside of the mercury pools proper are not indicative of the evaporation temperature of the mercury. The temperature was, therefore, calculated from the amount of heat carried off by the cooling water. This amount was determined by measuring the temperature of the inflowing and outflowing cooling water and its rate.

Density determinations were made by the same picnometer method described in a previous

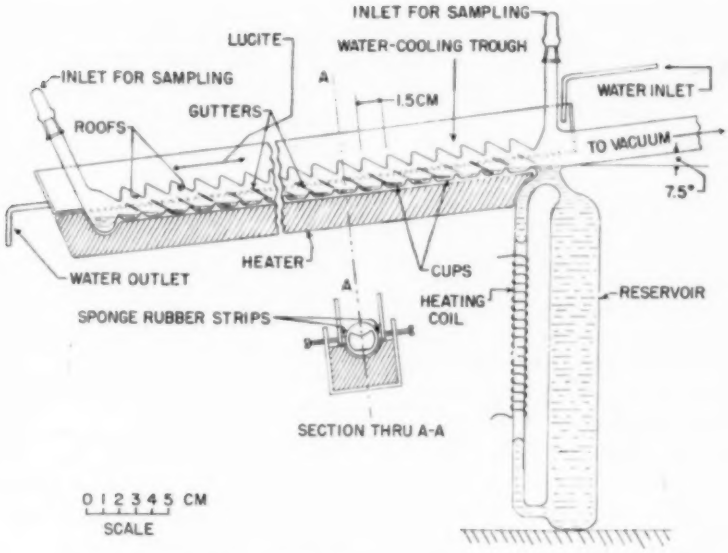


FIGURE 1. *All-glass column for the concentration of isotopes of mercury.*

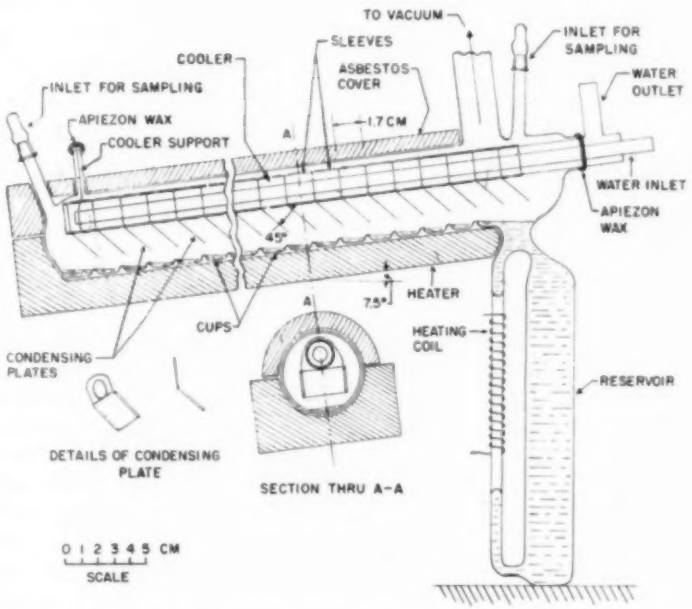


FIGURE 2. *Glass column with internal metal cooler for the concentration of isotopes of mercury*

paper [1]. In cases where operation of the column was resumed after sampling, the mercury samples were first returned to the respective end or reservoir of the column, from which they were removed.

## IV. Experimental Work and Results

Column I was operated at 74° C for 256 hr. The operation was then stopped and samples drawn from the lower end of the column and from the reservoir for density measurements. Operation of the column was then continued for another 681 hr, i. e., for a total of 937 hr. Column II was operated at 100° C first for 546 hr and, after sampling from the lower end, it was operated at the same temperature for another 761 hr, a total of 1,307 hr. A sample was removed from the lower end, and operation was continued with a fresh batch of mercury at 76° C. This run lasted 408 hr, and a sample was then taken from the lower end of the column. Column III was operated at 100° C for three consecutive periods, 243, 500, and 507 hr. Samples were taken from both ends of the column after each period.

Experimental details and results of density determinations are shown in table 2. In columns I and II, which had large reservoirs at the upper ends, only the heavy isotopes were concentrated at the lower ends. The highest concentrations obtained were +117.3 and +107.0 ppm, in columns I and II, respectively. In column III, which was without a reservoir, the greatest difference in density between the light and heavy fractions was about 190 ppm. As seen from table 2, countercurrent fractionation had apparently reached equilibrium in the first 700 hr of operation.

TABLE 2. *Experimental details and results*

| Column | Experiment | Hg in reservoir or upper end of column | Hg in lower end of column. Heavy fraction | Duration of experiment | Temperature | Change in density of light fractions | Change in density of heavy fractions |
|---|---|---|---|---|---|---|---|
| | | *g* | *g* | *hr* | *° C* | *ppm* | *ppm* |
| I | 1 | 2,100 | 74 | 256 | 64 | 0 | 72.0 |
| | 2 | 2,100 | 74 | *937 | 66 | 0 | 117.3 |
| | | | | | | ---- | |
| II | 1 | 2,400 | 100 | 546 | 78 | ---- | 53.7 |
| | 2 | 2,400 | 100 | *1,307 | 78 | ---- | 107.0 |
| | 3 | 2,400 | 76 | 408 | 67 | ---- | 91.6 |
| III | 1 | 91 | 100 | 243 | ---- | −56.1 | 48.8 |
| | 2 | 91 | 100 | *743 | ---- | −102.8 | 86.9 |
| | 3 | 91 | 100 | *1,250 | ---- | −89.8 | 105.1 |

* Cumulative time including the hours of the experiment immediately above them.

The results of experiments shown in table 2 indicate an unsatisfactory performance for all the columns. A comparison of these results with those obtained in the 10-cell steel apparatus [1], under equilibrium conditions, shows that while in the 10-cell column change of density per cell was 18 ppm, the change in these columns was approximately 0.8, 1.0, and 3.2 ppm per cell for columns I, II, and III, respectively. The inability of the all-glass and glass-metal columns described here to separate isotopes of mercury efficiently can be explained in the following manner. The cells in these columns should not be considered as individual plates because of the fact that they were not separated from each other by partitions as was the case in the 10-cell steel column. The vapor over each pool of mercury had a chance to mix freely with the vapor over the neighboring pools above and below it. However, even under these conditions there should have been a greater separation of isotopes than was actually obtained. Even if two or three cells acted as one plate, the total change in density, for example, in column III should have been $(150/2)\times 18=1{,}350$ or $(150/3)\times 18=900$ ppm, on the basis of performance of the 10-cell steel column.

The chief difficulty was due, undoubtedly, to the small capacity of the mercury cups in the cells. This capacity was about 0.6 ml in columns I and III and about 0.9 ml in column II. In view of the high surface tension of Hg and its inability to wet glass, it did not drain regularly and uniformly from cup to cup along the column, so that some pools were filled more than others by as much as 100 percent or even more and some pools were observed to stay altogether empty for several hours at a time. In case of the 10-cell steel apparatus, where each cell had a capacity of about 9 ml, these irregularities of counterflow were minimized by the large volume of the liquid in each cell. In the present columns, where the capacity of each cell was from 1/15 to 1/10 of that in the 10-cell steel column, these irregularities had a critical effect on the operation. All-glass and glass-metal columns similar to those described in this paper were used for refluxing liquids with normal surface tension and having the ability to wet glass. On the basis

of 2 to 3 cells operating as one complete plate, these columns performed as well as the 10-cell steel column, where each cell operated as a plate.

## V. Mass-Spectrometer Analysis of Isotopic Ratios of Mercury Concentrates

Measurements of mercury isotope ratios were made on a 60° Nier type [6] mass spectrometer provided with a "continuous balance" recording potentiometer. The ionization chamber was constructed of copper; however, the copper ion-repeller, being in direct path of the Hg vapor beam, was replaced, as a precautionary step, with a fine platinum gauze.

The inlet system was in the form of a glass manifold to which six sample tubes could be attached. Each sample tube consisted of a 3-mm inside diameter tube attached to a 1-cm inside diameter tube, the small tube ending inside the larger tube in the form of a sealed capillary break-off projection. The Hg sample was introduced into the smaller tube through an open end. This end was then sealed to an evacuation system, the tube evacuated to about $10^{-6}$ mm Hg and then sealed off so as to enclose the Hg sample. The sample tube was then sealed on to the manifold by its 1-cm inside diameter open end. Admission of mercury vapor from the sample tube into the mass spectrometer was accomplished by dropping a magnetically manipulated iron ball, about 0.8 cm in diameter on the capillary break-off, inside the large part of the sample tube.

After evacuating the mass spectrometer and before dropping the iron ball on the break-off, the manifold was flamed until the largest peak on the Hg background was a small fraction of the recorder scale at the highest recorder sensitivity. The sample tube was then immersed in liquid air, the iron ball dropped on the break-off, and pumping continued for some time. The liquid air was then replaced with a freezing mixture at —23° C, and the measurements of isotope ratios were carried out while the sample was kept at this temperature. When a set of measurements was completed, the freezing mixture was replaced with liquid air again, and the smaller part of the sample tube holding the Hg sample was sealed off. Whenever necessary, venting of the mass-spectrometer chamber was accomplished by cracking off the manifold and not by opening a stopcock beyond the mercury-vapor pump and liquid-air trap, as is usually done in vacuum work. In this way the mass-spectrometer chamber remained free of Hg contamination from outside sources.

Analysis was made by successively comparing the heights of the recorder peaks from $^{198}$Hg to $^{202}$Hg with that of $^{204}$Hg. For each comparison the sequence, zero-$^{204}$Hg-zero-peak-zero-$^{204}$Hg-zero, was run 10 times, the scanning rate being set to cause the recorder pen to linger several seconds at the tip of each peak.

Eight samples of normal Hg were analyzed, and the average isotope ratios are shown in table 3 in comparison with those of Nier [4]. There seems to be a very good agreement between the two sets of ratios. No attempt was made to determine ratio $^{196}$Hg/$^{204}$Hg, since the height of the $^{196}$Hg peak is only about 2 percent of the $^{204}$Hg reference peak. The presence of a memory effect was checked by comparing analyses of five normal samples, each following analysis of a heavy sample, with those of three normal samples, each following a light sample. The small differences found were in the opposite direction to that which a memory effect would indicate. The results of all the isotope ratio determinations are shown in table 4.

Densities of the various mercury concentrates were calculated on the basis of the isotope ratios shown in table 4. A comparison between the experimentally determined density deviations of the concentrates from normal Hg and those calculated is given in table 5. On the basis of data in table 4, concentrations of $^{204}$Hg in samples III-3-L and III-3-H are found to be 6.684 and 6.899. This gives a total enrichment of $^{204}$Hg in the lowest cell of column III over that in the uppermost cell of 4.66 percent.

TABLE 3. *Abundance ratios of* Hg *isotopes*

Comparison between the present work and that of Nier

| Ratio measured | Values of isotope ratio | | |
|---|---|---|---|
| | Present work | Nier's work | Percentage deviation |
| 196/204 | ..... | 0.022 | ..... |
| 198/204 | 1.527 | 1.507 | −1.3 |
| 199/204 | 2.553 | 2.537 | −0.6 |
| 200/204 | 3.487 | 3.467 | −.6 |
| 201/204 | 1.971 | 1.965 | −.3 |
| 202/204 | 4.401 | 4.405 | +.1 |



798448—48——4

TABLE 4. *Mass spectrometer analysis of isotope ratios in mercury concentrates*

| Sample | Number of duplicates analyzed | Isotope ratios in normal Hg and in concentrates | | | | | |
|---|---|---|---|---|---|---|---|
| | | 196/204[a] | 198/204 | 199/204 | 200/204 | 201/204 | 202/204 |
| III-3-L[b] | 5 | 0.0231 | 1.572 | 2.619 | 3.525 | 2.005 | 4.426 |
| Normal | 8 | .0224 | 1.527 | 2.553 | 3.487 | 1.971 | 4.401 |
| II-1-H | 3 | .0213 | 1.475 | 2.493 | 3.390 | 1.925 | 4.374 |
| II-3-H | 3 | .0210 | 1.450 | 2.456 | 3.383 | 1.923 | 4.371 |
| III-3-H | 7 | .0206 | 1.436 | 2.425 | 3.341 | 1.907 | 4.365 |
| II-2-H | 3 | .0206 | 1.433 | 2.435 | 3.320 | 1.905 | 4.363 |

[a] Ratio 196/204 for normal Hg is that given by Nier, all the other ratios in this column were estimated by assuming that the amount of concentration of a given isotope was proportional to difference between the molecular weight of this isotope and the average molecular weight of Hg. This relationship was found to be approximately true for the other light isotopes.

[b] Roman numeral stands for column, arabic number for experiment, and L and H for light and heavy fraction (see table 2).

TABLE 5. *Comparison between experimental density values and those calculated from isotope ratio data for* Hg *concentrates*

| Sample | Deviation of density from normal, in ppm | | Percentage difference |
|---|---|---|---|
| | Experimental | Calculated | |
| III-3-L | −89.8 | −86.1 | −4.2 |
| II-1-H | +53.7 | +76.8 | +43.0 |
| II-3-H | +91.6 | +100.1 | +9.2 |
| III-3-H | +105.1 | +104.9 | −1.9 |
| II-2-H | +107.0 | +103.3 | −4.4 |

## VI. Conclusions

Concentration of $^{204}Hg$ in long countercurrent molecular distillation columns having small cups of less than 1 ml capacity, gave poor results, as compared with a 10-cell steel column with large cups, described in a previous publication. The chief reason lies in the fact that, because of the small hold-up in the cells, a liquid like Hg, with a very high surface tension did not reflux regularly, so that individual cells held more liquid at one time than at another. There are indications, however, that with liquids of normal surface tension, 2–3 cells in such columns act as one plate, comparable with one cell in the 10-cell steel columns. The all-glass and glass-metal columns described in this paper are more easily constructed and, where the liquid has a normal surface tension and refluxes regularly, a smaller hold-up is more advantageous.

Mass Spectrometer analyses of isotope ratios in normal Hg gave results that are in good agreement with those obtained by Nier. The mass spectrometer isotope enrichment determinations agree fairly well with direct density measurements by the picnometer method.

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# Determination of Lactose Alone and in the Presence of Sucrose by the Method of Munson and Walker

By Lester D. Hammond

The existence of uncertainties in the tables employed in the determination of lactose, alone and in the presence of sucrose, by the method of Munson and Walker has led to the redetermination of the reducing-sugar values from which these tables were calculated. The original tables were based on the weights of cuprous oxide corresponding to various weights of lactose, and in the present paper all values are referred to the weights of copper determined electrolytically. Data showing the magnitude of the contamination of the cuprous oxide under the conditions prevailing in the method are given. The table of Straughn and Given for mixtures of lactose and sucrose in the ratio of 1:12 is shown to be in error. From the redetermined values an extensive table of the copper values for lactose and for two ratios of lactose and sucrose has been computed.

## I. Introduction

The estimation of lactose is of considerable importance to the dairy industry, to other processors of food, and to the State and Federal Governments. The interest of the latter is indicated by the fact that the determination of lactose is listed in the Book of Methods of the Association of Official Agricultural Chemists.

This paper is a report of the results obtained by the redetermination of the copper values of lactose and two of its mixtures with sucrose by the unified method of Munson and Walker. This method, published in 1906 [1],[1] has found wide acceptance because of its simplicity and reproducibility of results. However, the original tables are based on the weight of cuprous oxide obtained rather than on the procedure of the direct determination of metallic copper or of other accepted methods. In addition, there exists evidence that there are other errors in these tables.

The original Munson and Walker table consisted of weights of dextrose, invert sugar, and two mixtures of invert sugar and sucrose corresponding to various weights of cuprous oxide. In 1907 Walker [2] extended the applicability of the method to include both lactose and maltose. Subsequently, an error in the calculation of the lactose table was discovered, and a corrected table was published [3] in 1912. In this same year Given published [4] a book of methods of sugar analysis in which he stated that a question had arisen as to the composition of the lactose prepared by Walker. He further stated that "Mr. M. N. Straughn of the Sugar Laboratory, Bureau of Chemistry, U. S. Dept. of Agric. has prepared a pure sugar and made the determinations for a new table for lactose, and with the assistance of the author has made the calculations for that table and, in addition, the determinations and calculations for a table for a mixture of 1 part lactose and 4 parts sucrose for use on condensed milks, and for 1 part lactose and 12 parts sucrose for use on milk chocolates. In all cases the work was done on lactose of the formula $5(C_{12}H_{22}O_{11})+2(H_2O)$, and calculated to the hydrated form $C_{12}H_{22}O_{11}+H_2O$." As far as can be ascertained, this direct quotation from Givens' book is the only record of this work extant. No statement was made as to the method of preparing the lactose, no analytical data were given, nor did the author state the method of determining copper, which, presumably, was weighed as $Cu_2O$ in the manner followed by Munson and Walker. As

[1] Figures in brackets indicate the literature references at the end of this paper.

this table for lactose and its mixtures with sucrose is official with the Association of Official Agricultural Chemists, it seemed desirable to carry out a complete redetermination on the basis of the copper values rather than on the basis of weights of cuprous oxide.

## II. Preparation of Lactose

Walker prepared his sample of lactose by pouring a hot aqueous solution of the recrystallized sugar into alcohol, with constant stirring. The fine crystals that separated were first dried in air and then over anhydrous calcium chloride. From a moisture determination according to the method of Brown, Morris, and Millar [5] on the dried purified sample, Walker concluded that the composition of his preparation was $C_{12}H_{22}O_{11} \cdot \frac{1}{2}H_2O$. This conclusion was further supported by a determination of carbon and hydrogen. He reported the specific rotation of his material to be 52.93°, but did not specify the concentration, temperature, or wavelength. Von Lippman [6] states that lactose prepared in the manner described above has the composition $5C_{12}H_{22}O_{11} \cdot 2H_2O$. Quisumbing and Thomas [7] prepared lactose by adding equal volumes of alcohol and ether to a cold aqueous solution of sugar. They report moisture (loss at 125° to 130°) 5.22 percent, ash 0.03 percent and $[\alpha]_D^{25}=52.90°$. Lane and Eynon [8] prepared lactose by recrystallizing a pure commercial sample twice from water and found the specific rotation to be 52.5°. Bertrand [9] recrystallized lactose five times from an aqueous solution and found $[\alpha]_D^{19}=54.5°$. He declared the sample to be $C_{12}H_{22}O_{11} \cdot H_2O$. Schmoeger [10] showed that the specific rotation of lactose hydrate for c=2.372 to 41.536 was independent of the concentration and from a mean of 70 determinations found that $[\alpha]_D^{20}=52.53°$. This value was confirmed by Deniges and Bonvans [11] as well as by Parcus and Tollens [12] and it is the value reported in NBS Circular C440. On the contrary, Bacharach [13] determined the value 52.42°, which agrees with the value given by Grossman and Bloch [14]. Hudson [15] has demonstrated that lactose prepared by precipitating with alcohol is not a definite compound, but that it is a mechanical mixture of the hydrated and anhydrous forms. Given and Walker state that their analytical work was done on lactose having a known formula, and that the results were calculated to $C_{12}H_{22}O_{11} \cdot H_2O$. Quisumbing and Thomas made no statement as to the composition of their preparation. They gave its physical constants, apparently regarded it as the monohydrate, and reported their analytical results on that basis. However, from the work of Hudson it seems possible that the differences in the specific rotation values of these various preparations were due to differences in the amount of water of hydration.

The lactose used in this work was prepared from U. S. P. lactose. A hot 50-percent solution was treated with vegetable char and filtered. Aluminum hydroxide was then added, the solution filtered, and the filtrate was crystallized while in motion. This material was then twice recrystallized under the following conditions. A 50-percent solution was made by heating to 80° C. The temperature was maintained around this point to prevent the formation of β-lactose, which is stable above 93° C. The solution was crystallized in motion while cooling it to room temperature. The mother liquor was separated from the crystals by means of a centrifuge, and the crystals were washed with water at 5° C and dried at room temperature. The lower part of a desiccator was filled with a large portion of the dried material, and a working sample of the lactose was stored over it. The desiccator was kept in a room at 20° C. At the same time, a small weighed sample of the lactose was placed in the desiccator and kept exposed to its atmosphere. This sample has remained at constant weight over a period of months. Analysis showed the preparation to contain: moisture, 5.05 percent; ash, 0.003 percent; and $[\alpha]_D^{20}$ (c=6.9779)=52.54°. These data indicate that the material is lactose monohydrate, $C_{12}H_{22}O_{11} \cdot H_2O$.

## III. Contamination of Cuprous Oxide

It has long been known that $Cu_2O$, produced by the action of impure solutions of reducing sugar such as sugar-house products, is contaminated with organic and inorganic impurities. It is not so generally appreciated, however, that $Cu_2O$, formed by the reducing action of solutions of pure sugars, is contaminated with organic impurities, for the

[2] McDonald and Turcotte [16] have recently completed an extensive study of α-lactose hydrate, in which they determined the loss of weight in vacuum at 80°, 120°, and 130° C. The curves show that this hydrate contains 5 percent of water of hydration. However, they observed a slight variation in the total loss of weight and in the discoloration of the sample with change in time and temperature.

statement is commonly found in the literature that copper should be weighed as $Cu_2O$ only when pure sugars are involved. Before Munson and Walker [1] expressed the results of their work in terms of the weight of $Cu_2O$, the senior author [17] made a series of determinations on solutions of an unidentified reducing sugar in which series the copper was determined electrolytically and as $Cu_2O$. He obtained differences between the two sets that varied between $-1.2$ and $+1.8$ mg. A surprising thing about these differences is the fact that in a series of 29 copper determinations, the results from the electrolytic set were higher than those weighed as $Cu_2O$ in 18 determinations, three sets giving identical weights. Munson states that a portion of the differences can be attributed to the loss of weight of the Gooch crucibles caused by the solvent action of Soxhlet's reagent on the asbestos. No details of the work are given and it may be surmised that, during the electrolysis, the current density may have been such that the deposit of copper was oxidized. Munson concluded from this work, however, that copper could be determined as $Cu_2O$ when solutions of pure sugar were used.

Shortly after the publication of Munson and Walker's work, Zerban and Naquin [18], using a solution of invert sugar and the Munson and Walker method, compared the copper values calculated from the weights of $Cu_2O$ and CuO with the corresponding values determined by Low's volumetric iodide method. The results from the CuO and volumetric sets were practically identical but were 2 mg lower than those from $Cu_2O$. This difference they attributed to incomplete drying of the $Cu_2O$. They used the Monroe crucible [19] and thus missed the visual evidence of the contamination of the $Cu_2O$ by organic decomposition products, which is readily observed in a porcelain crucible when the $Cu_2O$ is treated with nitric acid.

When the reducing sugar values of the Munson and Walker method were redetermined by the author [20] and compared with the original ones, it was noted that differences existed between the two sets of data that were greater than any that could be attributed to probable experimental error. Jackson and McDonald [21] made a comprehensive study of these differences and showed that the amount of contamination of the $Cu_2O$ was almost exactly equal to the differences between the copper values of Munson and Walker and the newly determined ones. They also emphasized that the copper that is reduced should not be determined by weighing it as cuprous oxide. It seemed desirable to investigate the extent of the contamination of the cuprous oxide when lactose and mixtures of lactose and sucrose are evaluated.

Determinations of various concentrations of lactose and its mixtures with sucrose were made by weighing the copper as $Cu_2O$, then dissolving it in nitric acid and determining the copper electrolytically. The data in table 1 are the differences between the value of the copper calculated from the weight of $Cu_2O$ and the value of the copper determined electrolytically. In all cases, the value of the electrolytic copper is the smaller and, as is to be expected, the differences increase with increasing concentrations of sugar. This effect is much less pronounced with lactose, however, than with its sucrose mixtures.

TABLE 1. *Contamination of cuprous oxide*

| Weight of lactose-$H_2O$ | Lactose-$H_2O$ | Lactose-$H_2O$ and sucrose | |
|---|---|---|---|
| | | 1 lactose 4 sucrose | 1 lactose 12 sucrose |
| *mg* | *mg of* Cu | *mg of* Cu | *mg of* Cu |
| 60 | ..... | ..... | 0.2 |
| 100 | ..... | 0.1 | .5 |
| 140 | ..... | .7 | ..... |
| 150 | ..... | ..... | 2.1 |
| 200 | 0.1 | 1.3 | 3.3 |
| 240 | ..... | 1.9 | ..... |
| 250 | .4 | ..... | 4.9 |
| 300 | .6 | 2.8 | ..... |
| 305 | ..... | ..... | 7.5 |
| 340 | ..... | 3.8 | 9.1 |
| 350 | .8 | ..... | ..... |

## IV. Analytical Procedure

The basic conditions of the determination as given by Munson and Walker were followed. The Soxhlet reagent contained 34.639 g of $CuSO_4.5H_2O$ in 500 ml and 173 g of potassium sodium tartrate ($KNaC_4H_4O_6.4H_2O$) and 50 g of sodium hydroxide in 500 ml. The sucrose used was National Bureau of Standards Standard Sample 17. The preparation and properties of the lactose used have been given in detail above. All solutions were measured at 20° C.

In the original method, the solution was heated over a gas flame, but in this work electrical heating was substituted. The heater was of such a type that the solution in the beaker was practi-

cally surrounded by the heating element and the current was controlled by means of a constant-voltage regulator and a variable ratio transformer. The solution could be brought to boiling in the required time within ±5 sec.

The determinations were made as follows: 50 ml of the solution containing lactose was transferred to a 400-ml beaker containing 50 ml of the mixed Soxhlet reagent. The solution was heated to the boiling point in 4 min and then allowed to boil 2 min longer. The cuprous oxide was transferred immediately to a Gooch crucible and washed with water at 60° C. It was then dissolved by adding 5 ml of 1:1 nitric acid, and the crucible was quickly covered. Before the addition of the acid a small quantity of water was added to the crucible to minimize the ebullition of nitric oxides. The copper nitrate and washing were received in a 250-ml beaker to which 10 ml of the 1:1 nitric acid and about 5 g of ammonium sulfate had been added. Sufficient water was added to cover the cylindrical platinum-gauze electrodes, the total volume of electrolyte being about 180 ml. The electrolysis was conducted overnight at room temperature and at an approximate current density of 0.10 amp/dm². Upon completion of the deposition, the electrolyte was replaced by distilled water before the circuit was broken. The copper was washed with alcohol, dried 15 min at 100° C, cooled in a desiccator, and then weighed. All deposits were bright and showed no evidence of oxidation.[3]

The copper values given in table 2 are the average of four aliquots from one solution of a given concentration. Sugar concentrations above and below those employed in good analytical procedure were included in order to establish the direction of the curve for the whole range of concentrations and particularly in the region where the concentration of copper in the reacting mixture becomes diminishingly small.

## V. Calculation of Results and Sugar Tables

An examination of the experimental data shown in table 2 shows that a modified equation for the rectangular hyperbola will fit the data satisfactorily. The equation

$$(a+x)(b-y)=c+d(y_1-y)^{-1} \quad (1)$$

is formed by adding the term $(d(y_1-y)^{-1}$ to the equation for the rectangular hyperbola and was developed by J. B. Saunders of this Bureau in connection with previous work of the author [20]. In this equation, $x$ equals milligrams of sugar and $y$ equals milligrams of copper. As the concentration of sugar increases, the curve bends more and more away from the copper ordinate, and the added term allows the curve to approach the limiting value of copper in the reagent, $y_1$=440.9 mg, asymptotically. The applicability of the Munson and Walker method is questionable for concentrations of sugar corresponding to values of copper greater than approximately 395 mg and it probably would be more desirable to limit the maximum sugar concentration of determinations within a range of about 200 to 250 mg in 50 ml.

From the average result of each series of determinations as shown in table 2, the constants of eq 1 were calculated and adjusted by the method of averages, and the values of the adjusted constants are given in table 3.

TABLE 2. *Experimental data*

| Weight of lactose.$H_2O$ taken | Weight of Cu found | | |
|---|---|---|---|
| | Lactose.$H_2O$ | Lactose.$H_2O$ and sucrose | |
| | | 1 lactose 4 sucrose | 1 lactose 12 sucrose |
| *mg* | *mg* | *mg* | *mg* |
| 10 | 12.6 | ..... | ..... |
| 20 | 25.8 | 26.5 | 28.2 |
| 40 | 52.5 | 52.9 | 57.0 |
| 60 | 78.2 | 79.9 | 85.2 |
| 80 | 104.3 | 106.8 | 112.9 |
| 100 | 129.6 | 133.2 | 140.3 |
| 120 | 156.4 | 160.0 | 167.9 |
| 140 | 182.4 | 185.5 | 194.5 |
| 160 | 207.8 | 211.9 | 220.9 |
| 180 | 232.7 | 237.7 | 247.4 |
| 200 | 259.5 | 263.6 | 274.5 |
| 220 | 285.2 | 289.8 | 300.8 |
| 240 | 309.9 | 315.8 | 326.9 |
| 260 | 335.9 | 342.5 | 352.8 |
| 280 | 361.0 | 366.7 | 377.7 |
| 300 | 385.2 | 391.5 | 403.5 |
| 320 | 409.8 | 416.4 | 428.3 |
| 340 | 435.4 | 439.3 | 439.3 |
| 360 | 439.6 | 439.8 | 439.7 |

[3] In determining the copper values upon which to base the table, the electrolytic method of estimating copper was selected because of its extreme accuracy. In the routine analysis of products containing lactose, any of the conventional methods of determining copper may be used.

TABLE 3. *Values of equation constants*

| Constants | Lactose. $H_2O$ | Lactose. $H_2O$ and sucrose mixtures | |
|---|---|---|---|
| | | 1 lactose 4 sucrose | 1 lactose 12 sucrose |
| $a$ | 16, 922. 8 | 11, 123. 61 | 5, 504. 99 |
| $b$ | 22, 207. 2 | 14, 979. 37 | 7, 812. 13 |
| $c$ | 375, 810, 000 | 166, 628, 700 | 43, 001, 550 |
| $d$ | 492, 005 | 246, 657 | 176, 400 |

Solving eq 1 for $x$ it becomes

$$x=\frac{c+d(y_1-y)^{-1}}{b-y}-a, \qquad (2)$$

where $x$ equals milligrams of sugar, $y$ equals milligrams of copper and $y_1$ equals 440.9, the amount of copper in milligrams in 50 ml of the alkaline tartrate copper reagent. The number of significant figures retained in the parameters was found sufficient to eliminate any significant computational errors in table 7.

Table 4 shows the differences between the experimental values and those computed from eq 2. For the whole range of experimental points in the determination of lactose and of its mixtures with sucrose, the mean differences are fairly small. However, considering the practical working range of the method not to exceed 280 mg of sugar, the differences between the experimental and computed values become 0.2 mg each for the three sets of determinations.

In table 5 are shown the differences in terms of milligrams of copper between the tables of Walker and those of Straughn and Given and the data in table 7. The comparisons are made for various increments of lactose, as shown in column 1. The data of Straughn and Given are from table 78 of NBS Circular C440, which had been calculated to copper from the original values reported in weights of $Cu_2O$. They were then corrected for the organic impurities in the $Cu_2O$ by means of a graph constructed from data in table 1. For lactose and its mixture with sucrose in the ratio of 1:4, the differences between the various sets are moderate, but the differences given in column 5 are greater than could reasonably be attributed to differences caused by experimental errors. As shown in column 5, the difference for the concentration of 40 mg of lactose is about the same as the others, but as the sugar concentration increases the differences become correspondingly larger. Since there is no record of the work of Straughn and Given other than their table of copper and

TABLE 4. *Differences between the experimental and computed values*

| Lactose .$H_2O$ | | | Sucrose and lactose .$H_2O$ | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 1 lactose; 4 sucrose | | | 1 lactose; 12 sucrose | | |
| Weight taken | Weight calculated | Weight calculated minus weight taken | Weight taken | Weight calculated | Weight calculated minus weight taken | Weight taken | Weight calculated | Weight calculated minus weight taken |
| *mg* | *mg* | *mg* | *mg* | *mg* | *mg* | *mg* | *mg* | *mg* |
| 20 | 19.8 | −0.2 | 20 | 20.0 | 0 | 20 | 19.5 | −0.5 |
| 40 | 40.2 | .2 | 40 | 39.7 | −0.3 | 40 | 40.0 | 0 |
| 60 | 59.9 | −.1 | 60 | 60.0 | 0 | 60 | 60.2 | 0.2 |
| 80 | 80.0 | 0 | 80 | 80.2 | 0.2 | 80 | 80.3 | .3 |
| 100 | 99.5 | −.5 | 100 | 100.1 | .1 | 100 | 100.2 | .2 |
| 120 | 120.2 | .2 | 120 | 120.4 | .4 | 120 | 120.5 | .5 |
| 140 | 140.3 | .3 | 140 | 139.8 | −.2 | 140 | 140.1 | .1 |
| 160 | 160.0 | 0 | 160 | 160.0 | 0 | 160 | 159.8 | −.2 |
| 180 | 179.4 | −.6 | 180 | 179.7 | −0.3 | 180 | 179.6 | −.4 |
| 200 | 200.3 | .3 | 200 | 199.6 | −.4 | 200 | 200.1 | .1 |
| 220 | 220.4 | .4 | 220 | 219.8 | −.2 | 220 | 220.1 | .1 |
| 240 | 239.7 | −.3 | 240 | 240.0 | 0 | 240 | 240.1 | .1 |
| 260 | 260.2 | .2 | 260 | 260.7 | 0.7 | 260 | 260.1 | .1 |
| 280 | 280.0 | 0 | 280 | 279.7 | −.3 | 280 | 279.5 | −.5 |
| 300 | 299.2 | −.8 | 300 | 299.2 | −.8 | 300 | 299.9 | −.1 |
| 320 | 319.0 | −1.0 | 320 | 319.0 | −1.0 | 320 | 320.7 | .7 |
| 340 | 342.6 | 2.6 | 340 | 343.0 | 3.0 | 340 | 342.4 | 2.4 |
| Mean | ---------- | 0.5 | ---------- | ---------- | 0.5 | ---------- | ---------- | 0.4 |

sugar equivalents, any explanation of the cause of these differences must be speculative. However, if their lactose is considered to be anhydrous and their concentrations calculated to the hydrate, the differences between the copper values of the recalculated concentrations and those in table 7 are much smaller and are given in column 6. They are on the order of the other differences shown in this table. It can only be surmised that, due to some inadvertence, the Straughn and Given copper equivalents for the mixture of lactose and sucrose in the ratio of 1:12 are those for the anhydrous form instead of those for lactose monohydrate.

TABLE 5. *Differences between the various lactose tables*

| Weight lactose .$H_2O$ | Copper values | | | | |
|---|---|---|---|---|---|
| | Lactose .$H_2O$ | | Sucrose and lactose .$H_2O$ | | |
| | Walker minus Hammond | Straughn-Given minus Hammond | 1 lactose 4 sucrose (Straughn-Given minus Hammond) | 1 lactose 12 sucrose (Straughn-Given minus Hammond) | 1 lactose 12 sucrose (Straughn-Given (corrected) minus Hammond)* |
| *mg* | *mg* | *mg* | *mg* | *mg* | *mg* |
| 40 | 2.8 | 2.1 | 2.7 | 2.3 | ..... |
| 60 | 2.4 | 2.0 | 2.7 | 4.3 | −0.1 |
| 80 | 1.8 | 1.9 | 2.8 | 6.1 | .3 |
| 100 | 1.4 | 1.7 | 2.6 | 7.9 | .7 |
| 120 | 1.0 | 1.7 | 2.4 | 9.4 | .9 |
| 140 | 0.5 | 1.5 | 2.1 | 10.9 | 1.0 |
| 160 | 0 | 1.5 | 1.9 | 12.2 | 1.0 |
| 180 | −0.5 | 1.3 | 1.8 | 13.4 | 0.8 |
| 200 | −1.0 | 1.2 | 1.3 | 14.3 | .7 |
| 220 | −1.7 | 0.9 | 1.0 | 15.3 | .3 |
| 240 | −2.3 | .9 | 0.6 | 15.9 | −.1 |
| 260 | −2.7 | .5 | .3 | 16.5 | −.9 |
| 280 | −3.3 | .4 | −.2 | 17.1 | −1.1 |
| 300 | −3.8 | .4 | −.7 | 17.7 | −1.7 |
| 320 | −3.8 | .7 | −.6 | ..... | −1.2 |

* This column shows the differences between the values of Straughn and Given and those of table 7 when it is assumed that their lactose is anhydrous and when calculated to hydrate.

Table 7 was calculated by means of eq 2. It shows the sugar values of lactose hydrate and two of its mixtures with sucrose for weights of copper from 10 to 435 mg in intervals of 1 mg. For lactose the slope of the curve changes so slowly that, for the first 300 points, linear interpolations could be made between values calculated from eq 2 at 50-point intervals. Between 300 and 375 mg, the calculated intervals were 25 points apart, and from 375 mg each point was calculated. For the 1:4 ratio the first 200 points were linearly interpolated at calculated intervals of 50 mg; from 200 to 375 mg of copper each tenth point was calculated and thence each point. For the 1:12 mixture each tenth point between 100 and 375 mg was calculated, as well as each individual point after 375 mg.

## VI. General Discussion

Since there is no stoichiometrical relation between the reacting compounds in a determination of reducing sugar by the use of Soxhlet's reagent, it follows that all such determinations must be empirical. In order to utilize these reactions as a quantitative analytical method, it is necessary that all procedures and conditions be standardized and to observe rigidly all such conditions of the method when making a determination. Then, in order to be able to interpret the results, it is required that certain data accompany the method. They are usually given in the form of a table, such as table 7. In its present form this table has a limited use. Although the Straughn-Given table was published in 1912, no proposal was made to widen its use until 1930 when White [22] published a graph constructed from the data in this table. In 1932 Fitelson [23] also published a graph based on that of White's to which he added an additional curve and extrapolated all the curves to include the 16:1 ratio of sucrose to lactose, and since 1935 this chart has been included in the Methods of Analysis of the Association of Official Agricultural Chemists. Following the present procedure, the author has already completed some work of extending the ratios of sucrose to lactose in convenient intervals from 2:1 to 20:1, inclusive, so as to secure more extended data from which to construct a chart or table for correcting determinations of lactose in mixtures with sucrose for the presence of the sucrose. It is expected that this work will be completed and published in the near future.

TABLE 6. *Comparison with results of Hammond*

| | Milligrams of lactose taken | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 20 | 40 | 50 | 100 | 150 | 200 | 260 | 300 |
| | Milligrams of copper found | | | | | | | |
| Hammond | 25.8 | 52.5 | ..... | 129.6 | ..... | 259.5 | 335.9 | 385.2 |
| Brewster | 25.7 | 52.6 | 65.5 | 130.4 | 194.8 | 259.4 | 335.4 | 386.2 |
| Computed from table 7 | 26.1 | 52.3 | 65.3 | 130.3 | 194.7 | 259.1 | 335.8 | 386.3 |

TABLE 7. *Table for calculating lactose hydrate and its mixtures with sucrose*

| Copper | Lactose .$H_2O$ | Lactose .$H_2O$ and sucrose | |
|---|---|---|---|
| | | 1 lactose 4 sucrose | 1 lactose 12 sucrose |
| *mg* | *mg* | *mg* | *mg* |
| 10 | 7.7 | 7.7 | 6.6 |
| 11 | 8.5 | 8.5 | 7.3 |
| 12 | 9.3 | 9.2 | 8.0 |
| 13 | 10.0 | 10.0 | 8.7 |
| 14 | 10.8 | 10.7 | 9.4 |
| 15 | 11.5 | 11.5 | 10.1 |
| 16 | 12.3 | 12.2 | 10.8 |
| 17 | 13.1 | 12.9 | 11.5 |
| 18 | 13.8 | 13.7 | 12.2 |
| 19 | 14.6 | 14.4 | 12.9 |
| 20 | 15.4 | 15.2 | 13.6 |
| 21 | 16.1 | 15.9 | 14.4 |
| 22 | 16.9 | 16.7 | 15.1 |
| 23 | 17.7 | 17.4 | 15.8 |
| 24 | 18.4 | 18.2 | 16.5 |
| 25 | 19.2 | 18.9 | 17.2 |
| 26 | 19.9 | 19.7 | 17.9 |
| 27 | 20.7 | 20.4 | 18.6 |
| 28 | 21.5 | 21.1 | 19.3 |
| 29 | 22.2 | 21.9 | 20.0 |
| 30 | 23.0 | 22.6 | 20.7 |
| 31 | 23.8 | 23.4 | 21.4 |
| 32 | 24.5 | 24.1 | 22.2 |
| 33 | 25.3 | 24.9 | 22.9 |
| 34 | 26.1 | 25.6 | 23.6 |
| 35 | 26.8 | 26.4 | 24.3 |
| 36 | 27.6 | 27.1 | 25.0 |
| 37 | 28.4 | 27.9 | 25.7 |
| 38 | 29.1 | 28.6 | 26.4 |
| 39 | 29.9 | 29.4 | 27.1 |
| 40 | 30.6 | 30.1 | 27.8 |
| 41 | 31.4 | 30.8 | 28.6 |
| 42 | 32.2 | 31.6 | 29.3 |
| 43 | 32.9 | 32.3 | 30.0 |
| 44 | 33.7 | 33.1 | 30.7 |
| 45 | 34.5 | 33.8 | 31.4 |
| 46 | 35.2 | 34.6 | 32.1 |
| 47 | 36.0 | 35.3 | 32.8 |
| 48 | 36.8 | 36.1 | 33.5 |
| 49 | 37.5 | 36.8 | 34.3 |
| 50 | 38.3 | 37.6 | 35.0 |
| 51 | 39.1 | 38.3 | 35.7 |
| 52 | 39.8 | 39.1 | 36.4 |
| 53 | 40.6 | 39.8 | 37.1 |
| 54 | 41.4 | 40.6 | 37.8 |
| 55 | 42.1 | 41.3 | 38.5 |
| 56 | 42.9 | 42.1 | 39.3 |
| 57 | 43.7 | 42.8 | 40.0 |
| 58 | 44.4 | 43.6 | 40.7 |
| 59 | 45.2 | 44.3 | 41.4 |
| 60 | 46.0 | 45.1 | 42.1 |
| 61 | 46.7 | 45.8 | 42.8 |
| 62 | 47.5 | 46.5 | 43.6 |
| 63 | 48.3 | 47.3 | 44.3 |
| 64 | 49.0 | 48.0 | 45.0 |

TABLE 7. *Table for calculating lactose hydrate and its mixtures with sucrose*—Continued

| Copper | Lactose .$H_2O$ | Lactose .$H_2O$ and sucrose | |
|---|---|---|---|
| | | 1 lactose 4 sucrose | 1 lactose 12 sucrose |
| *mg* | *mg* | *mg* | *mg* |
| 65 | 49.8 | 48.8 | 45.7 |
| 66 | 50.6 | 49.5 | 46.4 |
| 67 | 51.3 | 50.3 | 47.1 |
| 68 | 52.1 | 51.0 | 47.9 |
| 69 | 52.9 | 51.8 | 48.6 |
| 70 | 53.6 | 52.5 | 49.3 |
| 71 | 54.4 | 53.3 | 50.0 |
| 72 | 55.2 | 54.0 | 50.7 |
| 73 | 55.9 | 54.8 | 51.4 |
| 74 | 56.7 | 55.5 | 52.2 |
| 75 | 57.5 | 56.3 | 52.9 |
| 76 | 58.2 | 57.0 | 53.6 |
| 77 | 59.0 | 57.8 | 54.3 |
| 78 | 59.8 | 58.5 | 55.0 |
| 79 | 60.5 | 59.3 | 55.7 |
| 80 | 61.3 | 60.0 | 56.5 |
| 81 | 62.1 | 60.8 | 57.2 |
| 82 | 62.8 | 61.6 | 57.9 |
| 83 | 63.6 | 62.3 | 58.6 |
| 84 | 64.4 | 63.1 | 59.3 |
| 85 | 65.1 | 63.8 | 60.1 |
| 86 | 65.9 | 64.6 | 60.8 |
| 87 | 66.7 | 65.3 | 61.5 |
| 88 | 67.4 | 66.1 | 62.2 |
| 89 | 68.2 | 66.8 | 62.9 |
| 90 | 69.0 | 67.6 | 63.7 |
| 91 | 69.7 | 68.3 | 64.4 |
| 92 | 70.5 | 69.1 | 65.1 |
| 93 | 71.3 | 69.8 | 65.8 |
| 94 | 72.1 | 70.6 | 66.5 |
| 95 | 72.8 | 71.3 | 67.3 |
| 96 | 73.6 | 72.1 | 68.0 |
| 97 | 74.4 | 72.8 | 68.7 |
| 98 | 75.1 | 73.6 | 69.4 |
| 99 | 75.9 | 74.3 | 70.2 |
| 100 | 76.7 | 75.1 | 70.9 |
| 101 | 77.4 | 75.8 | 71.6 |
| 102 | 78.2 | 76.6 | 72.3 |
| 103 | 79.0 | 77.3 | 73.1 |
| 104 | 79.7 | 78.1 | 73.8 |
| 105 | 80.5 | 78.8 | 74.5 |
| 106 | 81.3 | 79.6 | 75.2 |
| 107 | 82.1 | 80.4 | 76.0 |
| 108 | 82.8 | 81.1 | 76.7 |
| 109 | 83.6 | 81.9 | 77.4 |
| 110 | 84.4 | 82.6 | 78.1 |
| 111 | 85.1 | 83.4 | 78.9 |
| 112 | 85.9 | 84.1 | 79.6 |
| 113 | 86.7 | 84.9 | 80.3 |
| 114 | 87.4 | 85.6 | 81.0 |
| 115 | 88.2 | 86.4 | 81.8 |
| 116 | 89.0 | 87.1 | 82.5 |
| 117 | 89.8 | 87.9 | 83.2 |
| 118 | 90.5 | 88.6 | 84.0 |
| 119 | 91.3 | 89.4 | 84.7 |

TABLE 7. *Table for calculating lactose hydrate and its mixtures with sucrose*—Continued

| Copper | Lactose .$H_2O$ | Lactose .$H_2O$ and sucrose | |
|---|---|---|---|
| | | 1 lactose 4 sucrose | 1 lactose 12 sucrose |
| *mg* | *mg* | *mg* | *mg* |
| 120 | 92.1 | 90.2 | 85.4 |
| 121 | 92.8 | 90.9 | 86.1 |
| 122 | 93.6 | 91.7 | 86.9 |
| 123 | 94.4 | 92.4 | 87.6 |
| 124 | 95.2 | 93.2 | 88.3 |
| 125 | 95.9 | 93.9 | 89.0 |
| 126 | 96.7 | 94.7 | 89.8 |
| 127 | 97.5 | 95.5 | 90.5 |
| 128 | 98.2 | 96.2 | 91.2 |
| 129 | 99.0 | 97.0 | 92.0 |
| 130 | 99.8 | 97.7 | 92.7 |
| 131 | 100.6 | 98.5 | 93.4 |
| 132 | 101.3 | 99.2 | 94.1 |
| 133 | 102.1 | 100.0 | 94.9 |
| 134 | 102.9 | 100.7 | 95.6 |
| 135 | 103.6 | 101.5 | 96.3 |
| 136 | 104.4 | 102.3 | 97.1 |
| 137 | 105.2 | 103.0 | 97.8 |
| 138 | 106.0 | 103.8 | 98.5 |
| 139 | 106.7 | 104.5 | 99.3 |
| 140 | 107.5 | 105.3 | 100.0 |
| 141 | 108.3 | 106.0 | 100.7 |
| 142 | 109.0 | 106.8 | 101.4 |
| 143 | 109.8 | 107.5 | 102.2 |
| 144 | 110.6 | 108.3 | 102.9 |
| 145 | 111.4 | 109.1 | 103.6 |
| 146 | 112.1 | 109.8 | 104.4 |
| 147 | 112.9 | 110.6 | 105.1 |
| 148 | 113.7 | 111.3 | 105.8 |
| 149 | 114.4 | 112.1 | 106.6 |
| 150 | 115.2 | 112.8 | 107.3 |
| 151 | 116.0 | 113.6 | 108.0 |
| 152 | 116.8 | 114.4 | 108.8 |
| 153 | 117.5 | 115.1 | 109.5 |
| 154 | 118.3 | 115.9 | 110.2 |
| 155 | 119.1 | 116.6 | 111.0 |
| 156 | 119.9 | 117.4 | 111.7 |
| 157 | 120.6 | 118.2 | 112.4 |
| 158 | 121.4 | 118.9 | 113.2 |
| 159 | 122.2 | 119.7 | 113.9 |
| 160 | 122.9 | 120.4 | 114.6 |
| 161 | 123.7 | 121.2 | 115.4 |
| 162 | 124.5 | 121.9 | 116.1 |
| 163 | 125.3 | 122.7 | 116.8 |
| 164 | 126.0 | 123.5 | 117.6 |
| 165 | 126.8 | 124.2 | 118.3 |
| 166 | 127.6 | 125.0 | 119.1 |
| 167 | 128.4 | 125.7 | 119.8 |
| 168 | 129.1 | 126.5 | 120.5 |
| 169 | 129.9 | 127.3 | 121.3 |
| 170 | 130.7 | 128.0 | 122.0 |
| 171 | 131.5 | 128.8 | 122.7 |
| 172 | 132.2 | 129.5 | 123.5 |
| 173 | 133.0 | 130.3 | 124.2 |
| 174 | 133.8 | 131.1 | 124.9 |

TABLE 7. *Table for calculating lactose hydrate and its mixtures with sucrose*—Continued

| Copper | Lactose .$H_2O$ | Lactose .$H_2O$ and sucrose | |
|---|---|---|---|
| | | 1 lactose 4 sucrose | 1 lactose 12 sucrose |
| *mg* | *mg* | *mg* | *mg* |
| 175 | 134.6 | 131.8 | 125.7 |
| 176 | 135.3 | 132.6 | 126.4 |
| 177 | 136.1 | 133.4 | 127.2 |
| 178 | 136.9 | 134.1 | 127.9 |
| 179 | 137.7 | 134.9 | 128.6 |
| 180 | 138.4 | 135.6 | 129.4 |
| 181 | 139.2 | 136.4 | 130.1 |
| 182 | 140.0 | 137.2 | 130.8 |
| 183 | 140.8 | 137.9 | 131.6 |
| 184 | 141.5 | 138.7 | 132.3 |
| 185 | 142.3 | 139.4 | 133.1 |
| 186 | 143.1 | 140.2 | 133.8 |
| 187 | 143.9 | 141.0 | 134.5 |
| 188 | 144.6 | 141.7 | 135.3 |
| 189 | 145.4 | 142.5 | 136.0 |
| 190 | 146.2 | 143.3 | 136.8 |
| 191 | 147.0 | 144.0 | 137.5 |
| 192 | 147.7 | 144.8 | 138.2 |
| 193 | 148.5 | 145.5 | 139.0 |
| 194 | 149.3 | 146.3 | 139.7 |
| 195 | 150.1 | 147.1 | 140.5 |
| 196 | 150.8 | 147.8 | 141.2 |
| 197 | 151.6 | 148.6 | 142.0 |
| 198 | 152.4 | 149.3 | 142.7 |
| 199 | 153.2 | 150.1 | 143.4 |
| 200 | 153.9 | 150.9 | 144.2 |
| 201 | 154.7 | 151.6 | 144.9 |
| 202 | 155.5 | 152.4 | 145.7 |
| 203 | 156.3 | 153.2 | 146.4 |
| 204 | 157.0 | 153.9 | 147.1 |
| 205 | 157.8 | 154.7 | 147.9 |
| 206 | 158.6 | 155.5 | 148.6 |
| 207 | 159.4 | 156.2 | 149.4 |
| 208 | 160.2 | 157.0 | 150.1 |
| 209 | 160.9 | 157.7 | 150.9 |
| 210 | 161.7 | 158.5 | 151.6 |
| 211 | 162.5 | 159.3 | 152.4 |
| 212 | 163.3 | 160.0 | 153.1 |
| 213 | 164.0 | 160.8 | 153.8 |
| 214 | 164.8 | 161.6 | 154.6 |
| 215 | 165.6 | 162.3 | 155.3 |
| 216 | 166.4 | 163.1 | 156.1 |
| 217 | 167.1 | 163.9 | 156.8 |
| 218 | 167.9 | 164.6 | 157.6 |
| 219 | 168.7 | 165.4 | 158.3 |
| 220 | 169.5 | 166.2 | 159.1 |
| 221 | 170.3 | 166.9 | 159.8 |
| 222 | 171.0 | 167.7 | 160.6 |
| 223 | 171.8 | 168.5 | 161.3 |
| 224 | 172.6 | 169.2 | 162.1 |
| 225 | 173.4 | 170.0 | 162.8 |
| 226 | 174.2 | 170.8 | 163.6 |
| 227 | 174.9 | 171.5 | 164.3 |
| 228 | 175.7 | 172.3 | 165.1 |
| 229 | 176.5 | 173.1 | 165.8 |

TABLE 7. *Table for calculating lactose hydrate and its mixtures with sucrose*—Continued

| Copper | Lactose .$H_2O$ | Lactose .$H_2O$ and sucrose | |
|---|---|---|---|
| | | 1 lactose 4 sucrose | 1 lactose 12 sucrose |
| *mg* | *mg* | *mg* | *mg* |
| 230 | 177.3 | 173.8 | 166.5 |
| 231 | 178.1 | 174.6 | 167.3 |
| 232 | 178.8 | 175.3 | 168.0 |
| 233 | 179.6 | 176.1 | 168.8 |
| 234 | 180.4 | 176.9 | 169.5 |
| 235 | 181.2 | 177.6 | 170.3 |
| 236 | 181.9 | 178.4 | 171.0 |
| 237 | 182.7 | 179.2 | 171.8 |
| 238 | 183.5 | 180.0 | 172.5 |
| 239 | 184.3 | 180.7 | 173.3 |
| 240 | 185.1 | 181.5 | 174.0 |
| 241 | 185.8 | 182.3 | 174.8 |
| 242 | 186.6 | 183.0 | 175.5 |
| 243 | 187.4 | 183.8 | 176.3 |
| 244 | 188.2 | 184.6 | 177.0 |
| 245 | 189.0 | 185.3 | 177.8 |
| 246 | 189.7 | 186.1 | 178.5 |
| 247 | 190.5 | 186.9 | 179.3 |
| 248 | 191.3 | 187.6 | 180.1 |
| 249 | 192.1 | 188.4 | 180.8 |
| 250 | 192.9 | 189.2 | 181.6 |
| 251 | 193.6 | 189.9 | 182.3 |
| 252 | 194.4 | 190.7 | 183.1 |
| 253 | 195.2 | 191.5 | 183.8 |
| 254 | 196.0 | 192.2 | 184.6 |
| 255 | 196.8 | 193.0 | 185.3 |
| 256 | 197.5 | 193.8 | 186.1 |
| 257 | 198.3 | 194.6 | 186.8 |
| 258 | 199.1 | 195.3 | 187.6 |
| 259 | 199.9 | 196.1 | 188.3 |
| 260 | 200.7 | 196.9 | 189.1 |
| 261 | 201.4 | 197.6 | 189.8 |
| 262 | 202.2 | 198.4 | 190.6 |
| 263 | 203.0 | 199.2 | 191.4 |
| 264 | 203.8 | 199.9 | 192.1 |
| 265 | 204.6 | 200.7 | 192.9 |
| 266 | 205.3 | 201.5 | 193.6 |
| 267 | 206.1 | 202.2 | 194.4 |
| 268 | 206.9 | 203.0 | 195.1 |
| 269 | 207.7 | 203.8 | 195.9 |
| 270 | 208.5 | 204.6 | 196.7 |
| 271 | 209.2 | 205.3 | 197.4 |
| 272 | 210.0 | 206.1 | 198.2 |
| 273 | 210.8 | 206.9 | 198.9 |
| 274 | 211.6 | 207.6 | 199.7 |
| 275 | 212.4 | 208.4 | 200.4 |
| 276 | 213.2 | 209.2 | 201.2 |
| 277 | 214.0 | 210.0 | 202.0 |
| 278 | 214.7 | 210.7 | 202.7 |
| 279 | 215.5 | 211.5 | 203.5 |
| 280 | 216.3 | 212.3 | 204.2 |
| 281 | 217.1 | 213.0 | 205.0 |
| 282 | 217.9 | 213.8 | 205.7 |
| 283 | 218.7 | 214.6 | 206.5 |
| 284 | 219.4 | 215.4 | 207.3 |

TABLE 7. *Table for calculating lactose hydrate and its mixtures with sucrose*—Continued

| Copper | Lactose .$H_2O$ | Lactose .$H_2O$ and sucrose | |
|---|---|---|---|
| | | 1 lactose 4 sucrose | 1 lactose 12 sucrose |
| *mg* | *mg* | *mg* | *mg* |
| 285 | 220.2 | 216.1 | 208.0 |
| 286 | 221.0 | 216.9 | 208.8 |
| 287 | 221.8 | 217.7 | 209.5 |
| 288 | 222.6 | 218.4 | 210.3 |
| 289 | 223.3 | 219.2 | 211.1 |
| 290 | 224.1 | 220.0 | 211.8 |
| 291 | 224.9 | 220.8 | 212.6 |
| 292 | 225.7 | 221.5 | 213.4 |
| 293 | 226.5 | 222.3 | 214.1 |
| 294 | 227.3 | 223.1 | 214.9 |
| 295 | 228.0 | 223.9 | 215.6 |
| 296 | 228.8 | 224.6 | 216.4 |
| 297 | 229.6 | 225.4 | 217.2 |
| 298 | 230.4 | 226.2 | 217.9 |
| 299 | 231.2 | 227.0 | 218.7 |
| 300 | 232.0 | 227.7 | 219.5 |
| 301 | 232.7 | 228.5 | 220.2 |
| 302 | 233.5 | 229.3 | 221.0 |
| 303 | 234.3 | 230.1 | 221.7 |
| 304 | 235.1 | 230.8 | 222.5 |
| 305 | 235.9 | 231.6 | 223.3 |
| 306 | 236.7 | 232.4 | 224.0 |
| 307 | 237.4 | 233.1 | 224.8 |
| 308 | 238.2 | 233.9 | 225.6 |
| 309 | 239.0 | 234.7 | 226.3 |
| 310 | 239.8 | 235.5 | 227.1 |
| 311 | 240.6 | 236.3 | 227.9 |
| 312 | 241.4 | 237.0 | 228.6 |
| 313 | 242.2 | 237.8 | 229.4 |
| 314 | 243.0 | 238.6 | 230.2 |
| 315 | 243.7 | 239.4 | 230.9 |
| 316 | 244.5 | 240.1 | 231.7 |
| 317 | 245.3 | 240.9 | 232.5 |
| 318 | 246.1 | 241.7 | 233.2 |
| 319 | 246.9 | 242.5 | 234.0 |
| 320 | 247.7 | 243.2 | 234.8 |
| 321 | 248.5 | 244.0 | 235.5 |
| 322 | 249.2 | 244.8 | 236.3 |
| 323 | 250.0 | 245.6 | 237.1 |
| 324 | 250.8 | 246.3 | 237.8 |
| 325 | 251.6 | 247.1 | 238.6 |
| 326 | 252.4 | 247.9 | 239.4 |
| 327 | 253.2 | 248.7 | 240.1 |
| 328 | 253.9 | 249.5 | 240.9 |
| 329 | 254.7 | 250.2 | 241.7 |
| 330 | 255.5 | 251.0 | 242.4 |
| 331 | 256.3 | 251.8 | 243.2 |
| 332 | 257.1 | 252.6 | 244.0 |
| 333 | 257.9 | 253.3 | 244.8 |
| 334 | 258.7 | 254.1 | 245.5 |
| 335 | 259.4 | 254.9 | 246.3 |
| 336 | 260.2 | 255.7 | 247.1 |
| 337 | 261.0 | 256.5 | 247.8 |
| 338 | 261.8 | 257.2 | 248.6 |
| 339 | 262.6 | 258.0 | 249.4 |

TABLE 7. *Table for calculating lactose hydrate and its mixtures with sucrose*—Continued

| Copper | Lactose $H_2O$ | Lactose $H_2O$ and sucrose | |
|---|---|---|---|
| | | 1 lactose 4 sucrose | a lactose 12 sucrose |
| *mg* | *mg* | *mg* | *mg* |
| 340 | 263.4 | 258.8 | 250.2 |
| 341 | 264.2 | 259.6 | 250.9 |
| 342 | 265.0 | 260.4 | 251.7 |
| 343 | 265.8 | 261.1 | 252.5 |
| 344 | 266.6 | 261.9 | 253.3 |
| 345 | 267.4 | 262.7 | 254.0 |
| 346 | 268.1 | 263.5 | 254.8 |
| 347 | 268.9 | 264.2 | 255.6 |
| 348 | 269.7 | 265.0 | 256.4 |
| 349 | 270.5 | 265.8 | 257.1 |
| 350 | 271.3 | 266.6 | 257.9 |
| 351 | 272.1 | 267.4 | 258.7 |
| 352 | 272.9 | 268.2 | 259.4 |
| 353 | 273.7 | 268.9 | 260.2 |
| 354 | 274.4 | 269.7 | 261.0 |
| 355 | 275.2 | 270.5 | 261.8 |
| 356 | 276.0 | 271.3 | 262.6 |
| 357 | 276.8 | 272.1 | 263.3 |
| 358 | 277.6 | 272.8 | 264.1 |
| 359 | 278.4 | 273.6 | 264.9 |
| 360 | 279.2 | 274.4 | 265.7 |
| 361 | 280.0 | 275.2 | 266.4 |
| 362 | 280.8 | 276.0 | 267.2 |
| 363 | 281.6 | 276.8 | 268.0 |
| 364 | 282.4 | 277.5 | 268.8 |
| 365 | 283.2 | 278.3 | 269.6 |
| 366 | 284.0 | 279.1 | 270.3 |
| 367 | 284.8 | 279.9 | 271.1 |
| 368 | 285.6 | 280.7 | 271.9 |
| 369 | 286.3 | 281.5 | 272.7 |
| 370 | 287.1 | 282.2 | 273.5 |
| 371 | 287.9 | 283.0 | 274.2 |
| 372 | 288.7 | 283.8 | 275.0 |
| 373 | 289.5 | 284.6 | 275.8 |
| 374 | 290.3 | 285.4 | 276.6 |
| 375 | 291.1 | 286.2 | 277.4 |
| 376 | 291.9 | 286.9 | 278.2 |
| 377 | 292.7 | 287.7 | 278.9 |
| 378 | 293.5 | 288.5 | 279.7 |
| 379 | 294.3 | 289.3 | 280.5 |
| 380 | 295.0 | 290.1 | 281.3 |
| 381 | 295.8 | 290.9 | 282.1 |
| 382 | 296.6 | 291.7 | 282.9 |
| 383 | 297.4 | 292.4 | 283.6 |
| 384 | 298.2 | 293.2 | 284.4 |
| 385 | 299.0 | 294.0 | 285.2 |
| 386 | 299.8 | 294.8 | 286.0 |
| 387 | 300.6 | 295.6 | 286.8 |
| 388 | 301.4 | 296.4 | 287.6 |
| 389 | 302.2 | 297.2 | 288.4 |

TABLE 7. *Table for calculating lactose hydrate and its mixtures with sucrose*—Continued

| Copper | Lactose $H_2O$ | Lactose $H_2O$ and sucrose | |
|---|---|---|---|
| | | 1 lactose 4 sucrose | a lactose 12 sucrose |
| *mg* | *mg* | *mg* | *mg* |
| 390 | 303.0 | 298.0 | 289.2 |
| 391 | 303.8 | 298.8 | 290.0 |
| 392 | 304.6 | 299.5 | 290.7 |
| 393 | 305.4 | 300.3 | 291.5 |
| 394 | 306.2 | 301.1 | 292.3 |
| 395 | 307.0 | 301.9 | 293.1 |
| 396 | 307.8 | 302.7 | 293.9 |
| 397 | 308.6 | 303.5 | 294.7 |
| 398 | 309.4 | 304.3 | 295.5 |
| 399 | 310.2 | 305.1 | 296.3 |
| 400 | 311.0 | 305.9 | 297.1 |
| 401 | 311.8 | 306.7 | 297.9 |
| 402 | 312.6 | 307.5 | 298.7 |
| 403 | 313.4 | 308.3 | 299.5 |
| 404 | 314.2 | 309.1 | 300.3 |
| 405 | 315.0 | 309.9 | 301.1 |
| 406 | 315.9 | 310.7 | 301.9 |
| 407 | 316.7 | 311.5 | 302.7 |
| 408 | 317.5 | 312.3 | 303.5 |
| 409 | 318.3 | 313.1 | 304.3 |
| 410 | 319.1 | 313.9 | 305.1 |
| 411 | 319.9 | 314.7 | 305.9 |
| 412 | 320.7 | 315.5 | 306.7 |
| 413 | 321.6 | 316.3 | 307.6 |
| 414 | 322.4 | 317.1 | 308.4 |
| 415 | 323.2 | 317.9 | 309.2 |
| 416 | 324.0 | 318.7 | 310.0 |
| 417 | 324.9 | 319.5 | 310.8 |
| 418 | 325.7 | 320.3 | 311.7 |
| 419 | 326.5 | 321.2 | 312.5 |
| 420 | 327.4 | 322.0 | 313.4 |
| 421 | 328.2 | 322.8 | 314.2 |
| 422 | 329.1 | 323.6 | 315.0 |
| 423 | 329.9 | 324.5 | 315.9 |
| 424 | 330.8 | 325.3 | 316.8 |
| 425 | 331.7 | 326.2 | 317.6 |
| 426 | 332.6 | 327.0 | 318.5 |
| 427 | 333.5 | 327.9 | 319.4 |
| 428 | 334.4 | 328.8 | 320.4 |
| 429 | 335.3 | 329.7 | 321.3 |
| 430 | 336.3 | 330.6 | 322.3 |
| 431 | 337.3 | 331.5 | 323.3 |
| 432 | 338.3 | 332.5 | 324.4 |
| 433 | 339.4 | 333.5 | 325.5 |
| 434 | 340.7 | 334.6 | 326.7 |
| 435 | 342.0 | 335.8 | 328.1 |

Since there was a controversy over the composition of the lactose prepared by Walker, and since the author has discovered the Straughn-Given table for the lactose-sucrose ratio of 1:12 to be in error, it was felt that the results reported in this paper should not depend solely on the work of one individual. So the author has determined the reducing value of the lactose used by McDonald and Turcotte [16] in their work on the density and refractive index of lactose solutions and found it to be identical with that of his preparation. J. F. Brewster of this Bureau also prepared a sample of pure lactose and found its reducing power to be the same as that of McDonald and Turcotte and that of the author. In addition, he kindly checked several values in the experimental data given in table 2. His results are shown in table 6 and are self-explanatory.

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# Broad-and Narrow-Beam Attenuation of 500- to 1,400-Kilovolt X-Rays in Lead and Concrete[1]

By Harold O. Wyckoff, Robert J. Kennedy, and William R. Bradford

Both narrow- and broad-beam attenuation curves have been obtained for 500-, 600-, 800-, 1,000-, and 1,400-kilovolt X-rays in lead and concrete. For the experimental conditions used, it is shown that an irradiated area 12 inches in diameter for lead absorbers and 37 inches in diameter for concrete satisfy the barrier conditions required for broad-beam attenuation curves.

## I. Introduction

There have been numerous papers over the past 10 years dealing with X-ray protection in the range from 500 to 2,000 kv [1 to 6].[2] The data from these papers differ somewhat, because the conditions of the experiments were not always the same and therefore cannot be readily correlated. Part of this has been attributed to differences in the high-voltage wave form and inherent filtration for the several experimental arrangements used. Preliminary data [1 to 6] have indicated that the size of the irradiated area of the barrier may also be an important variable, but the magnitude and limits for this have not been explored quantitatively. The present report will deal with different sized beams of X-rays produced by direct-current potentials of 500, 600, 800, 1,000, and 1,400 kv with a transmission target. Barriers of lead and concrete will be considered. Concrete has been generally accepted in the energy range above about 500 kv where space is not important, because it is structurally self-supporting and relatively inexpensive. However, for applications requiring a minimum of thickness for a given protection, lead is still the most popular.

In the voltage range under consideration, X-rays are principally absorbed by the photoelectric and the Compton processes, since pair production is still relatively unimportant, even in lead for 1,400 kv. All of the photoelectric absorption and that part of the energy transferred to the Compton electrons are considered to be truly absorbed, since the electrons so produced have small likelihood of producing another X-ray photon. The part of the energy given to the scattered photon leaves the site of the encounter in a different direction from that of the incident photon. The amount of this energy retained by the scattered photon decreases with increase of the angle between the scattered and incident photons. Thus, if the beam is of small cross section, the scattered photons leave the incident bundle and will not be measured. If, however, the beam is of considerable width the photons scattered from the sides of the beam may enter a measuring volume situated near the center of the beam. The apparent attenuation of the beam, measured by the reduction in dosage rate in the barrier, may thus be greatly influenced by the inclusion of this scattered radiation.

One may think of the ionization produced in the ionization chamber placed on the far side of a protective barrier as being due to two different sources of radiation. (a) Part of the radiation comes directly from the target of the X-ray tube. (The target is essentially a point source for all practical dimensions used in protective studies). (b) The remainder of the measured dosage may come from a distributed source composed of the entire irradiated volume of the protective barrier. Several factors serve to limit the volume, which acts as this secondary source. The length of the incident plus the scattered photon path in the barrier will be greater for oblique rays and, there-

[1] This paper will also appear in Radiology.
[2] Figures in brackets indicate the literature references at the end of this paper.

fore, obliquely incident photons have a greater probability of being absorbed. In addition, the angle between these incident and scattered photons must be larger and, therefore, the scattered photon energy will be smaller. The latter factor, depending upon the atomic number of the protective barrier, may also increase the probability of true absorption. In the X-ray range here considered, this factor is not important for concrete but serves to limit the practical dimensions of the virtual source when lead barriers are used.

Another factor producing differences between measurements made with and without scattering has recently been described [8]. It was shown there that air ionization chambers are more sensitive to photons of energies below 70 kv than above. For increasing thickness of barrier, an equilibrium is soon established, so that as much of the low-energy radiation is absorbed as is created. As a result of this quality-dependent chamber sensitivity, one obtains an increase of dosage rate in protective barriers of low atomic number, such as concrete, where this low-energy radiation is not strongly absorbed. The attenuation curves are thus convex upward for small barrier thicknesses. On the other hand, for barriers of high atomic number such as lead, this effect is not observable, since the low-energy radiations are strongly absorbed in the barrier.

As can be easily seen from the above discussion, different experimental conditions may influence considerably the attenuation curve obtained. Two limiting conditions are thus defined for the work to be reported here. A narrow-beam attenuation curve shall be understood to be one where only a negligible amount of the scattered radiation from the barrier is measured in the ionization chamber. Practically, this condition amounts to having the irradiated area on the barrier subtend a small angle at the chamber. This condition may be verified experimentally by an inverse square check of the radiation received in the chamber. If the inverse square law is found to hold experimentally, with fixed position of the target and barrier but with variations of the target-to-chamber distance, then the contribution of scattered radiation from the barrier source is negligible.

Dosage readings—with a fixed position of the chamber, target, and barrier—are said to be for broad-beam conditions if, on increasing the irradiated area of the barrier, no increase in dosage rate is observed. This condition is, of course, only unique for that particular barrier-to-chamber distance. The above qualitative considerations indicate that the irradiated area required to fulfill broad-beam conditions will be larger for larger barrier-to-chamber distances. The requisite area may be reduced by shorter target-to-barrier distances and smaller chamber volumes.

Since some scattered radiation is measured by the chamber under broad-beam conditions but none is measured for narrow-beam conditions, the effective absorption coefficient must be different for the two conditions. The effective absorption coefficient is, however, proportional to the slope of the attenuation curve. Attenuation curves that include different amounts of scattered radiation in their determination should therefore have different slopes.

## II. Experimental Arrangement

The high-voltage generator and tube have been previously described [7]. Figure 1 shows the experimental arrangement for beam collimation and for dosage measurement. The filtration inherent in the X-ray tube was approximately 2.8 mm tungsten, plus 2.8 mm copper, plus 2.1 mm brass, plus 18.7 mm water for the center of the beam. The target protective housing consisted of a double-walled steel tank filled with lead shot to a thickness of approximately 6 in., and a 6-in. thick solid lead diaphragm. Three diaphragms of different apertures were used in the course of the experiments. They gave irradiated areas at the basement floor level whose diameters were approximately 13, 26, and 37 in., respectively. These dimensions were dictated on the lower end by the requirement of uniform irradiation of the chamber and on the upper end by a desire to minimize scattering from the pit walls.

Figure 2 shows a view of the pit in which the radiation measurements were made. The ionization chamber was connected to an evacuated cylinder housing an FP54 electrometer tube and a selection of resistors and could be moved by remote control both in azimuth and in elevation within the pit. (The chamber actually used had about one-twenty-fifth the volume of the one shown in fig. 2.) Remote switches controlled, and indicators defined, the position of the chamber in the pit, the resistor used, and the grid resistor boltage. The latter two figures, together with the volume

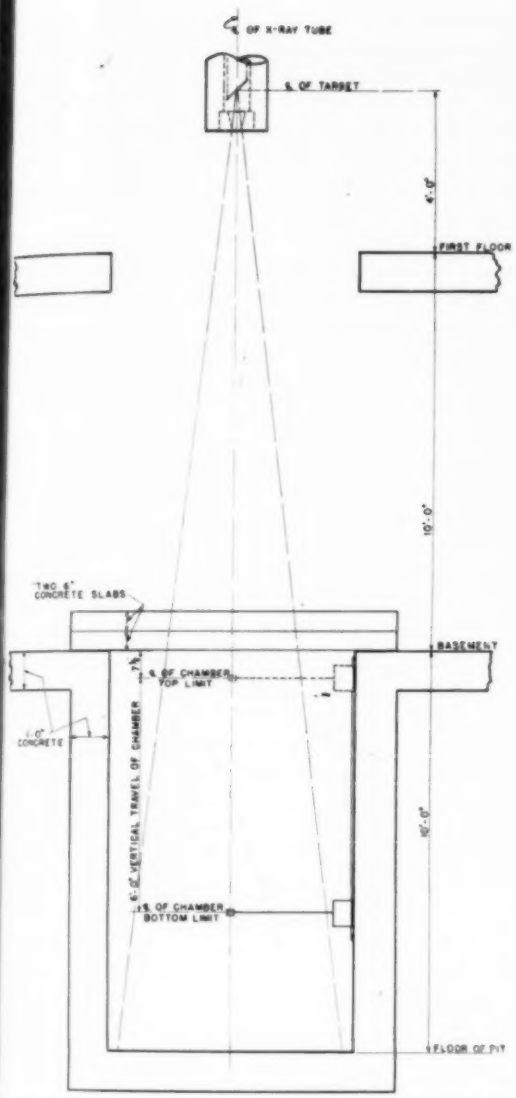


FIGURE 1. *Experimental arrangement for collimating the beam and for dosage measuremeni.*

of the chamber and the temperature and pressure of the air, served to determine the dosage rate. The chamber calibration determined from the value of the grid resistor, the grid voltage, and the mass of air in the chamber agrees to within 5 percent with that obtained experimentally with a standard radium source. By controlling the voltage and the current of the X-ray tube to within 0.1 percent, the X-ray dosage was found to be constant to 3 percent. A good share of this fluctuation in output could be attributed to random focal spot motion. It was not considered excessive for the present purposes.

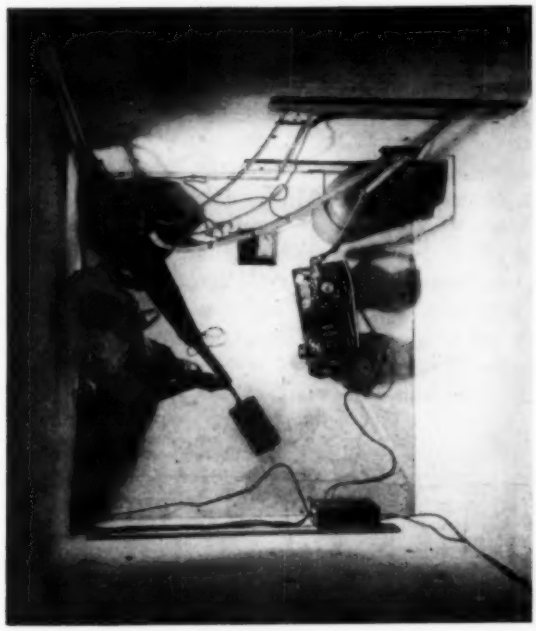

FIGURE 2. *Pit in which the measurements were made.*

For narrow-beam conditions, the absorbers were placed directly below the shield diaphragm. The chamber-to absorber distance could thus be varied from approximately 10 to 16 ft. The irradiated area of the samples was not more than 3 in. in diameter.

In testing for broad-beam conditions, the absorbers were laid directly over the top of the pit with an overlap of approximately 1 ft all around the lip. The concrete samples were in one piece, either 8 ft by 8 ft by 6 in. or 8 ft by 8 ft by 3 in. Lead samples were made up of 2 ft by 8 ft by ⅛ in. thick strips. Parallel strips covered the whole surface of the pit aperture in ⅛ in. thick layers. An overlap of at least ¼ in. was provided at each joint. Lap joints were staggered in adjacent layers, but none of the joints came closer than 9 in. to a line through the chamber and target. This lead, being quite flexible, required additional support. The pit aperture was reduced by placing plyboard on the basement floor extending over the pit. An unsupported area of lead 3 ft square was obtained in the center of the aperture. (This area



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was found to be adequate for broad-beam conditions with concrete. Smaller dimensions were expected and obtained for lead.)

The large concrete blocks were each weighed to an accuracy of 10 lb. Corrections were made for known air holes and reinforcing iron around the unexposed edges. Thicknesses of each slab, measured at a number of distributed points, were found to deviate by no more than ⅛ in. from their mean value. This mean thickness, together with the length, the width, and the corrected weight served to determine the average density. The mean of five additional thickness measurements obtained in the vicinity of the X-ray irradiated area was then corrected to correspond to a specific gravity of 147 lb/ft³ (2.35 g/cc). The narrow-beam concrete blocks are those previously used [10.] The accuracy of the concrete dimension measurements is estimated to be within 2 percent.

Approximately 300 measurements of thickness of the lead strips indicated maximum deviation from the mean of the order of ±4 percent.

All attenuation curves were obtained for a 7.5-in. chamber-to-barrier distance. This distance was a practical lower limit for our equipment. However, personnel are usually not located closer than 7.5 in. to the protective barrier in most medical X-ray installations. The target-to-chamber distance was thus 175½ in.

## III. Results

In order to properly evaluate this experiment, it was first necessary to investigate the extraneous scattering. Evidence of the lack of scattering without absorber may be obtained by observing the dosage rate at different distances from the target. The inverse square law may be used to reduce these dosage rates to a common distance. The variation of the values, so computed, is a measure of the amount of scattering present. Figure 7, A indicates the magnitude of the scattering. It is seen that, with no absorber in place and for the two smaller diaphragms, dosage rates computed back to a fixed distance (1 m) by the inverse square law remain essentially constant for large variations of the target-to-chamber distance. With the largest diaphragm, the main beam actually begins to strike the side walls about half way down the pit. The resultant scattering from the walls may contribute to the dosage rate measured in the center of the beam. Since the scattering is most important in the forward direction, some increase in the measured radiation should be obtained for chamber positions below the mid-depth of the pit. The experimental evidence verifies this qualitative prediction. Figure 7, A indicates that the contribution of scattering is about 5 percent of the main beam at a distance of 80 in. below the lip of the pit.

Scattered radiation will, of course, be measured with an absorber over the pit. The lack of extraneous scattering from the pit walls may be determined by measuring the radiation very near to the wall. If the radiation measured near to the wall is a small part of that in the center of the beam, then any contribution received at the center of the beam from the wall may be negligible. In figure 3 the pit walls correspond to angles of approximately −5° and 95°. The experimental results indicate that the dosage rate is rapidly decreasing as the walls are approached. The amount of radiation scattered from the nearer wall to the center of the beam is thus negligible. The dosage rate measured at the center of the beam and 7.5 in. from the absorber therefore does not include an appreciable amount of scattered radiation.

Figure 3 also indicates other interesting items. The sloped central portion of the azimuth curve without absorber has been discussed previously in the literature [9]. It may be attributed to change of the inherent filtration with angle. The asymmetry results from having the target

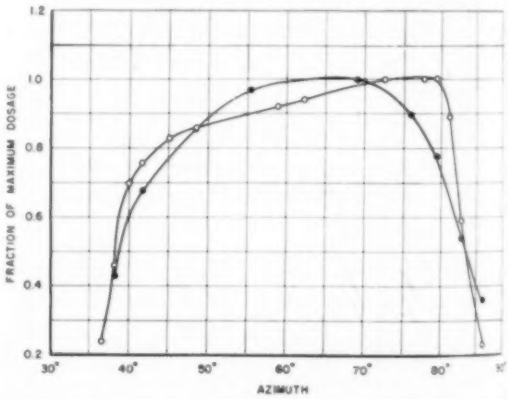


FIGURE 3. *Variation of dosage rate across the X-ray beam for an irradiated area approximately 37 in. in diameter.*

Open circles were obtained with no barrier. Filled circles were obtained with a 6-in.-thick concrete absorber in place.

set at 45° to the emergent beam. Large azimuth angles on this figure correspond to least inherent filtration. The figure also indicates that the presence of an absorber tends to sharpen the main peak but to increase the dosage rate near the foot of the curves. The first factor may be attributed to diminution of the beam by larger thicknesses of material at points different from the normal to the absorber. The second factor may be attributed to the radiation scattered out of the confines of the original beam.

It was found that each diaphragm gave a different apparent tube output. This increase in dosage rate with diaphragm size was attributed to spread of the focal spot. In order to show more clearly the effect of beam size on the attenuation curves, all dosage rates for a given diaphragm and kilovoltage have been reduced by the ratio of the apparent tube outputs—with zero absorber—for that disphragm and for the smallest diaphragm. All four sets of curves for a given voltage thus pass through the same zero absorber point.

Figure 4 shows the experimental attenuation curves for lead. The lower curve at each potential is for narrow-beam conditions. There was no important change in the data for irradiated areas greater than 13 in. in diameter. The actual deviation of the dosage rate for variation of the diaphragm was of the same order as the experi-

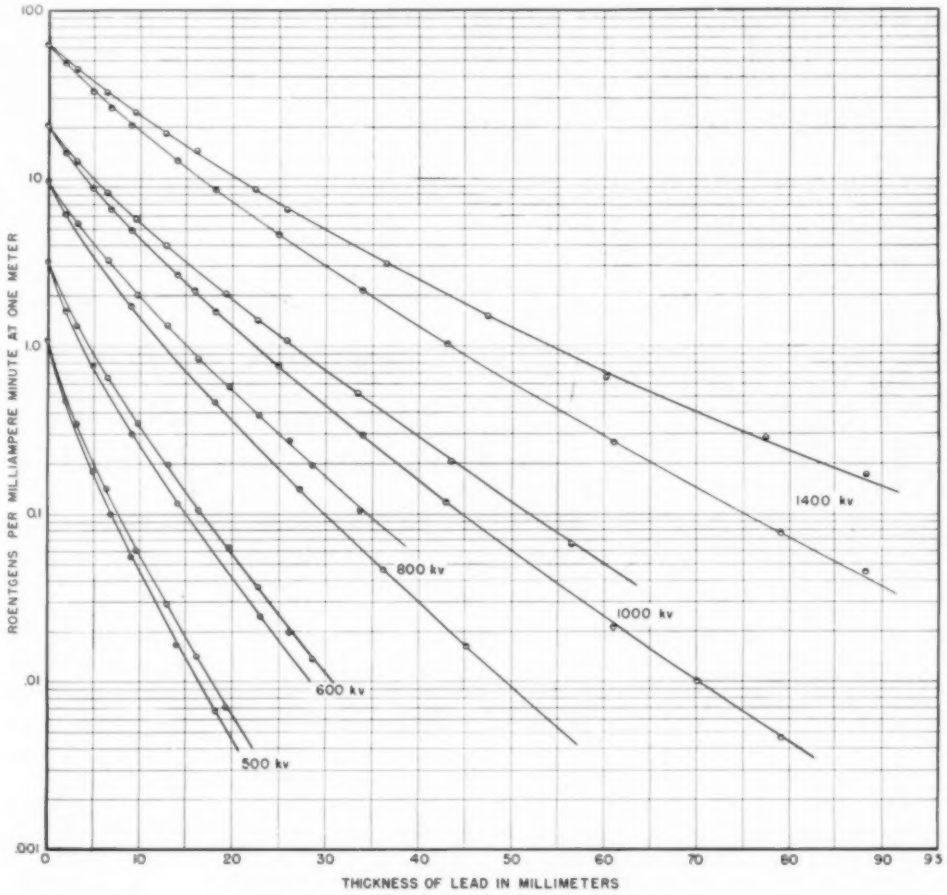


FIGURE 4. *X-ray attenuation curves in lead.*

Dosage rates for the three diaphragms under broad-beam conditions were so nearly the same that they could not be separated on this scale. ◒, Broad beams (diameter, 13 in.); ◓, narrow beam.

mental error. There is, however, an interesting change in the difference between narrow- and broad-beam absorption curves with potential producing the X-rays. In agreement with the qualitative predictions this difference becomes more important for large photon energies, since the scattered photons are not so readily absorbed photoelectrically.

Figures 5 and 6 show the attenuation curves for concrete. For each generator potential the lowest curve is for narrow-beam conditions, that is, when a negligible amount of the dosage is due to scattering from the absorber. The difference between successive curves with narrow-beam, 13, 26, and 37 in., irradiated diameter indicates the magnitude of the scattering from the corresponding ring of barrier. It is evident that the scattered

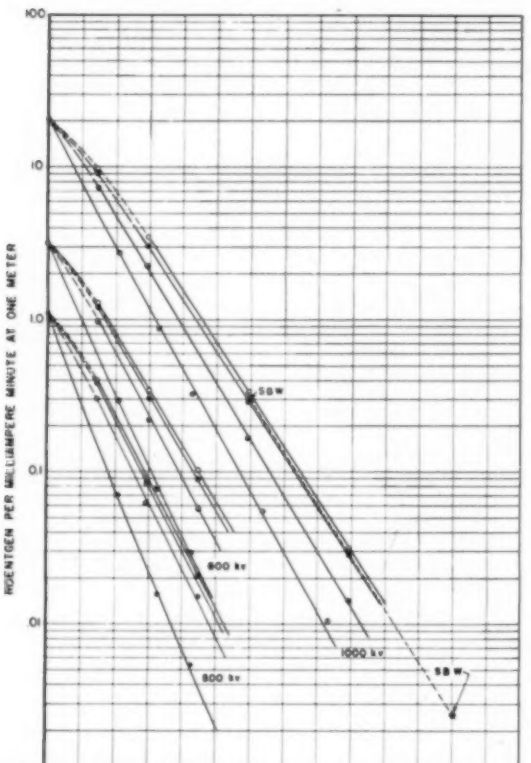


FIGURE 5. *X-ray attenuation curves in concrete.*

The density of the concrete is 147 lb/ft³. The dotted line is drawn through two experimental points obtained from published work of Singer, Braestrup, and Wyckoff with a resonance-type generator. ◓, Narrow beam; ◒, 13-in. beam; ●, 26-in. beam; ○, 37-in. beam.

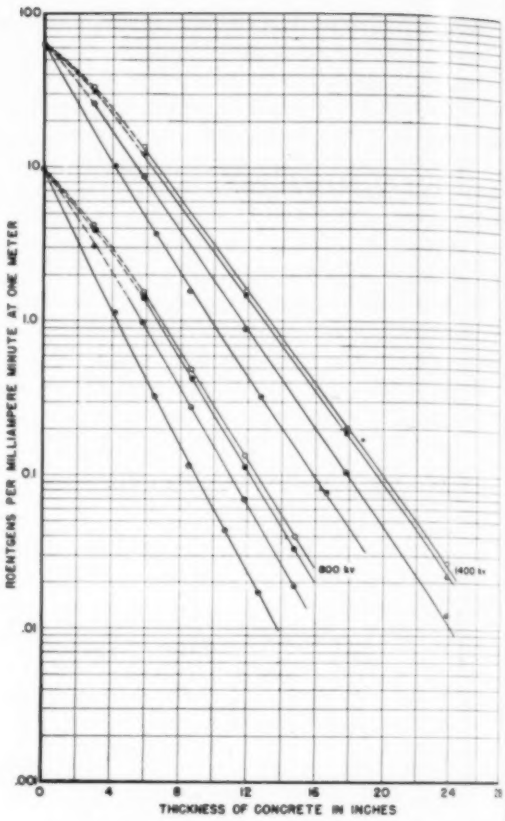


FIGURE 6. *X-ray attenuation curves in concrete.*

The density of the concrete is 147 lb/ft³. ◓, Narrow beam; ◒, 13-in. beam; ●, 26-in. beam; ○, 37-in. beam.

photons from the successive outer rings contribute less and less to the dosage rate measured on the axis of the beam. Because of the small change in dosage rate between the 26-in. and 37-in. beam and because of the rapidly decreasing contribution of scattering with beam size, the 37-in. diameter beam in concrete has been assumed for all practical purposes to correspond to broad-beam conditions under the experimental arrangement described above.

For comparison with data obtained from a resonance X-ray generator, two experimental points from Singer, Braestrup, and Wyckoff [1] have been included on figure 6. These were obtained with a two-million-volt resonance type unit operating at one million volts and giving an irradiated area of approximately 4½ ft by 7 ft.

The target-to-chamber distance was approximately 8 and 9 ft. These data have been corrected as nearly as possible to the experimental conditions used for our new data. The effect of the wave form on the X-ray output and the effect of the shorter target-barrier distance on the amount of the scattering measured in protection studies cannot be rigorously determined with our present knowledge. One may say, however, that the target current flows appreciably only when the alternating voltage peak is above 800 kv. The effective potential should therefore be somewhere between 800 and 1,000 kv. The slope of an attenuation curve is often taken as a measure of the effective potential of the X-rays. The points [1] give a line whose slope is midway between that here reported for 800 and 1,000 kv. The results are thus in qualitative agreement.

There is evidence, in the lead as well as the concrete curves, of a reduction in the slope of the attenuation curve with irradiated area. This effect is especially pronounced in the change from narrow beam to 13-in. diameter beam. There is also evidence in concrete, but not in lead, of the low energy scattered radiation. Both of these items tend to increase the barrier thickness requirements for broad beam over those for narrow beam.

Figure 7 for data taken at 1,000 kv, shows the importance of barrier-to-chamber distances. These curves were obtained by varying the elevation of the chamber in the pit. Figure 7, B is for a lead absorber placed over the pit. The three diaphragms all give essentially the same dosage rate at a distance of 7.5 in. below the absorber. Broad-beam conditions were therefore obtained at this position for an irradiated area of 13-in. diameter. As the barrier-to-chamber distance is increased, different diaphragms do not give the same dosage. Broad-beam conditions, therefore, do not exist in this intermediate region for the diaphragms used. At very large distances, the dosage rates appear to become constant. This condition corresponds to the requirements for narrow beam. As would be expected, the distance from the barrier for narrow-beam conditions increases with the size of the irradiated area. After correction for scattering, the dosage rate of the largest beam also agrees with that of the other beams at a distance of 78 in. Moreover, this constant dosage rate agrees with

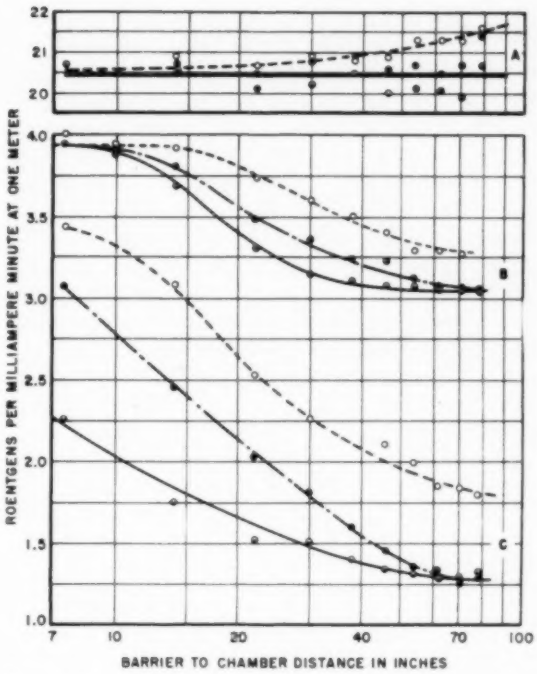


FIGURE 7. *Variation of X-ray dosage with distance from the lip of the pit for 1,000 kv.*

A, With no absorber in the beam; B, with 12.9 mm of lead over the pit; C, with 5.8 in. of concrete over the pit. ◒, 13-in. beam; ●, 26-in. beam: ○ 37-in. beam.

that obtained for the narrow-beam curves of figure 4. For the concrete sample indicated (fig. 7, C) it appears that the two smaller diaphragms approach narrow-beam conditions for a chamber-to-barrier distance of the order of 55 to 78 in. The dosage rate is here constant (1.3) and in agreement with the narrow-beam curve of figure 5, which also gives a value of 1.3 roentgens per milliampere minute at 1 m.

## IV. Conclusions

Because of the small irradiated areas required for broad-beam conditions in lead, the broad-beam attenuation curves should be used for nearly all cases where lead barriers are considered in this voltage range. The extra thickness of lead required for broad-beam conditions over that for narrow beam varies rapidly with X-ray tube potential. This extra thickness requirement varies from approximately 10 percent at 500 kv to 25 percent at 1,400 kv.

For concrete protective barriers, the difference between narrow- and broad-beam thickness requirements is of the order of 1½ to 2 half-value layers, depending upon the portion and kilovoltage of the curves considered. If the irradiated area of the barrier is not more than 3 ft in diameter, and if all personnel are restricted to distances larger than 10 ft from the barrier, then narrow-beam attenuation curves may be used in designing X-ray protection. Such restrictions are not usually feasible, however, because of space limitations. In addition, the cost of requiring the extra space may be larger than the saving in barrier cost.

For the majority of X-ray installation designs, therefore, the broad-beam attenuation curves should be used.

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# A Method for the Electron Microscopy of Wool[1]

By Max Swerdlow and Gloria S. Seeman

A simplified method for making shadowed thermoplastic negative replicas of fibrous materials was developed. Through this technique, fine details of the morphology of the wool fiber, before and after treatment, were clearly revealed by the electron microscope. The structural implications of the electron micrographs are discussed with respect to the subject of wear and in reference to the observations of other investigators.

## I. Introduction

### 1. The Problem

The electron microscope has been a useful tool for observing objects which are thin enough or which are sufficiently small and adequately dispersed to allow the proper scattering and transmission of electrons in the conventional 50-kv microscope.[2] The high resolving and magnifying powers of the electron microscope have thus been used with considerable success in the study of pigments, smokes, viruses, bacteria, and a variety of other colloidal particles. On the other hand, when efforts are made to study organic fibers such as wool, ordinary techniques of direct specimen preparation fail. In the first place, the fiber is too thick to transmit a sufficient intensity of electrons to excite the phosphor-coated screen into luminescence or to form an image on the photographic emulsion. At best only a profile view can be obtained when a section of the fiber is inserted in the specimen holder. Second, and no less troublesome, is the fact that in scattering most of the electron beam there is an exchange of energy. The subsequent generation of heat and electrostatic charges causes a charring and disintegration of the fiber itself. Third, the necessity of operating the electron microscope at a pressure of less than $10^{-4}$ mm of mercury results in dessication of the specimen. The literature of the past few years is replete with descriptions of limitations that make observation and interpretation difficult for the electron microscopist.

### 2. Evaluation of Existing Techniques

Partial solutions to the problem have been found by those concerned with the study of wool fibers. Fragments of triturated fibers of reduced and methylated wool are not adversely affected by the intense beam of electrons and are, in part, transparent to it. Such techniques, however, are very limited. Not only to they preclude getting detailed information about the surface structure of the fiber, but they eliminate the possibility of observing the same fiber before and after treatment because of the mechanical disorganization and chemical alteration that these techniques produce [1 to 6].[3]

The limitations of direct methods of surface observation by electron-optical means have led to the development of ingenious and diverse techniques for preparing thin film replicas of the surfaces of electron-optically "opaque" objects [7, 8]. The improvements and variations of the basic replica methods reported by a number of resourceful workers have been successfully applied to the study of many bulk materials [9, 10, 11]. None of these techniques, however, is easily applicable to the study of degraded wool fibers, since the use of excessive heat or crushing pressure in molding the replica introduces undesirable changes. Interpretation of results is often complicated by artifacts. Moreover, most replica methods involve

[1] This paper will also appear in the September issue of the Textile Research Journal.

[2] The RCA Type EMU electron microscope was used for this work.

[3] Figures in brackets indicate the literature references at the end of this paper

destruction of the specimen. This, too, eliminates the possibility of performing additional treatments on the same fiber.

In order, therefore, to augment the data on the structure of the wool fiber and to correlate these observations with results previously obtained by the direct disintegration of the fiber as well as by other methods, a simple, rapid, faithful replica technique was developed. This system of specimen preparation successfully combines methods useful for both optical and electron microscopy [12]. A negative replica of the wool fiber is made in a thermoplastic film which is thin enough to examine directly in the electron microscope and which may be shadow-cast, with a suitable metal for added contrast.

## II. Replica Method

### 1. Materials and Apparatus

Replicas can be made with two thermoplastic materials. One, ethyl cellulose,[4] is dissolved in ethyl acetate. Addition of about 10 percent of ethyl alcohol aids solution. The other thremoplastic, which yields a slightly stronger film and one that withstands electron bombardment better, is polystyrene.[5] Styron granules "dissolve" in benzene. Warming the solvent slightly hastens the reaction. Solutions of 1 to 2 percent (by weight) seem to be satisfactory for each resin. The principal criterion is the ability of the plastic films to transmit a sufficiently intense beam in the electron microscope. The films formed by evaporation of the solution after it is poured on to standard glass microscope slides are thicker than the substrate films usually employed for electron microscopy. About three-fourths of the slide is coated with the thermoplastic resin. The excess is drained off onto a towel by placing the glass slide in an almost vertical position. After 5 minutes of drying, a slightly wedge-shaped film, averaging about 0.4 micron in thickness, is formed.

The fibers to be studied should be rinsed in ethyl alcohol and/or ether to remove surface grease and dirt.[6] After being dried at room tempreature, these fibers are then singly placed upon the thermoplastic lacquer that is on the glass slide. Another glass microscope slide is then placed on top of the fibers, sandwiching them with the plastic film. This sandwich can be firmly held together with the aid of a C-clamp and a couple of strips of cardboard and heat-resistant rubber cut to fit the glass slides. Reasonable care must be exercised not to twist the assembly out of alinement. The rubber and cardboard pads take up most of the torque and contact pressure produced when the clamp screw is tightened, by hand, to the point where the sandwich will be firmly fixed without breaking the glass and without displacing the arrangement. The clamped glass sandwich of film and fibers is then heated in a laboratory resistance-type oven for about 20 minutes at 90° C. The film is thus softened to the point where it will flow and accept the wool fiber and form a faithful replica of the surfaces in contact with it.

The variable factors that affect the quality and resolution of the plastic replica are time, temperature, pressure, thickness of the film, and diameter of the fiber. If the thermoplastic is allowed to remain in the oven for too long or at too high a temperature, too much plastic flow and deformation will result. If too much pressure is applied, the displaced material will pile up on each side of the fiber and will disturb the quality and appearance of the replica (figs. 8 and 9). If the film is too thin for the diameter of the fiber, the fiber will be pushed through it to the glass and will prevent the plastic from molding itself about the fiber surface. To achieve the proper balance of all these elements is not a difficult problem, inasmuch as the limits of control are not critical. One or two trials ordinarily provide sufficient experience so that numerous acceptable replicas can be made in a comparatively short time. After the clamped sandwich is removed from the oven and allowed to cool to room temperature, it can be separated. Usually the wool fibers come away with the uncoated glass slide, leaving semicylindrical impressions in the plastic. If not, it is a simple matter to remove them whole with the aid of a fine brush or tweezers. These fibers having once been accurately molded can be saved for further chemical or physical treatment and subsequent replication.

### 2. Metallic Shadow-Casting

Metallic shadow-casting adds contrast as well as a three-dimensional aspect to the surface de-

[4] Sold commercially as Fxfilm, Ethocel, Ethofoil, etc.
[5] Styron made by Dow Chemical Co.
[6] The wool used for this work had been commercially degreased. Prolonged washing was, therefore, unnecessary.

tails of the replica [13, 14]. A very thin coating of evaporated chromium is deposited obliquely upon the plastic surface. The elevations and depressions of the surface replica cast characteristic shielded radiation shadows. Where no metal is condensed, transmission of the incident energy is a maximum. Where thick elevations and ridges occur coupled with a layer of metal, electron scattering is a maximum and little or no energy is transmitted.

The glass slide bearing the plastic film containing the replicas of the fibers is placed horizontally with the film side up in a vacuum chamber where it can be shadowed.[7] To prevent any appreciable heating, the thermoplastic replicas are placed a distance of 25 cm away from a conical basket made of 30-mil tungsten wire. The basket may be formed by winding the tungsten around the pointed end of a No. 10 wood screw. Heating the wire and screw helps to prevent brittle fracture during the winding process. If instead of the 30-mil wire a twisted double strand of 16- or 20-mil tungsten wire is used, no heat is required and it is easier to follow the troughs in the screw thread. The additional surface area provided by the stranded wire is advantageous. A 6-inch length of wire is sufficient for a basket about a centimeter high with leads of adequate length. The tungsten basket is set in the vacuum chamber so that the apex of the cone points downward and is 5 cm above the plane of the replica. A charge of 100 to 150 mg of pure chromium [8] metal fragments is placed in the basket. All of the metal is evaporated slowly with a current of 25 to 35 amperes at 10 to 15 volts in about 10 minutes at a pressure of $10^{-5}$ mm of mercury. A 10-minute outgassing period with 10 to 20 amperes running through the tungsten wire is a desirable practice.

The uniformity of deposition of the metal as it condenses on the specimen is a function of the mean free path and the accommodation coefficient. The latter depends upon the initial temperature, the emission temperature, and the striking temperature of the molecules or atoms of the metal. Given a large accommodation coefficient and a vacuum where the mean free path is about a meter in length, the molecules will traverse the distance from filament to specimen without collision and impinge upon the comparatively cold surface of the specimen with very high energy. If these conditions are not met, the molecules of metal will not stick where they land but will migrate, find other molecules, and form agglomerations of recrystallized metal. This produces a grainy, irregular deposition. At high magnification the poorly defined shadowed areas and the graininess of the surface provide undesirable effects.

[7] The RCA EMV unit was used for this work.

[8] Electrolytically deposited Chromium about 1/16 in. thick was used.

### 3. Selection and Examination

The chromium-shadowed thermoplastic negative replica, still on the glass slide, is viewed in an ordinary light microscope. Photomicrographs may now be taken, in the manner of Hardy and Plitt [12]. The replica may also be projected in a photoenlarger, in the manner of Scott and Wyckoff [15]. Or, desired areas may be selected and mounted for more detailed observation in the electron microscope. In the latter case, the woven, calendered, ¼-inch stainless steel, No. 200 U. S. Standard Sieve specimen screens are centered over the chosen areas of the replica, with the aid of a low-power light microscope. The screens usually adhere to the chromium coating, especially if contact is made with the convex side. No. 100- or 150-mesh screens would offer larger areas for observation. The glass slide bearing the replica film and the specimen screens is slowly immersed at almost grazing incidence into a 9-inch crystallizing dish of fresh tap water. The thermoplastic film can be readily floated off the glass slide with little or no teasing, especially if the edges of the glass slide where the plastic may have overrun are rubbed with the side of a dissecting needle or similar tool and no water is allowed to creep up over the film. The freely floating film supporting the specimen screens is removed from the water by flipping it over and out with a piece of paper about the size of a glass slide.

The screens are thereby lodged between the film and the paper. Any short-fibered paper may be used for this purpose. The short fibers prevent wrinkling and warping upon drying. Unprinted newspaper, porous filter paper, melamine resin-bonded map paper, blotting paper, or the strips used to separate the glass in a box of microscope slides may be used with about equal success. By using paper instead of glass to retrieve the floating film,[9] the specimen screens supporting

the selected areas of the replica can be readily removed after drying. To facilitate this, however, it is advisable to prick the film about the periphery of the screen with a needle point while the film and paper are still damp. A faster and easier technique which, however, involves some risk, is accomplished by spreading a small amount of a suitable solvent on glass and placing the dried paper in contact with it. The solvent soaks through the paper and to the plastic film. When the solvent evaporates, the paper is dried flat to the glass, the plastic is cemented to the paper, and the untouched areas of the replica supported by the specimen screens can be picked up with tweezers as easily as from a much thinner film. Obviously, if too much solvent is used the entire replica may be ruined. If a reasonable amount of caution is observed, however, this catastrophe will not occur. This technique provides a much more advantageous procedure for removing the specimen than any method of cutting or tearing the comparatively thick film from a hard glass slide or a coarse wire gauze.

Various workers in the field have suggested that a possible improvement in the technique for selecting and mounting the replica film on a specimen screen could be made by placing the film, replica side up, over a piece of 200-mesh wire cloth. After scanning the film for suitable areas with a light microscope, an auxiliary mount in the revolving nosepiece fitted with a cutting die could be turned into place and the tube racked down. In this manner, the desired area of film may be punched out with a supporting screen attached. The adaptation of a microscope-punch combination seems worthwhile not only for this work but in many other aspects of electron microscopy where systematic scanning is required for selecting areas of a prepared specimen.

## III. Application and Interpretation

The shadowed replica method was applied to the study of wool fibers as reflected by the characteristic changes after varying amounts of abrasion produced by an apparatus designed by Schiefer [16]. During the abrasion cycle fiber fragments fall from the abradant. This "debris", as well as the fibers bordering the hole worn through the woolen fabric, were examined. Hundreds of replicas were made of fibers abraded in this way. For comparison, replicas were made of untreated fibers, khaki-dyed fibers, as well as fibers subjected to chemical attack. The shadowed replicas were examined in the electron microscope at low magnifications obtained without the projector polepiece, as well as at the higher ranges of magnification. Electron micrographs were made with a 1-mil objective aperture and with 5- to 10-second exposure. Contact photographic reversals were made on another medium lantern slide plate for further optical enlargement. Negative prints are shown in the figures. For proper interpretation of the surface features of the negative replicas, they may be viewed as though they were obliquely illuminated. The "diameter" indicated in the micrographs represents 80 to 90 percent of the actual diameter of the wool fiber.

A wool fiber when plucked from the living animal consists of two distinct regions. The root is the living part and grows from the hair follicle. The nonliving portion that emerges from the root is called the shaft, which is the section shorn from the sheep and is here designated the wool fiber [17]. It generally consists of three principal concentric layers—a thin outer covering of scales (cuticle), a middle region (cortex), and a central core or pith (medulla). The relative thickness of each layer varies from fiber to fiber, as well as from sheep to sheep. In the very fine wool fibers the medulla is often absent, and a few comparatively large scales encircle the cortex. The spindle-shaped cortical cells comprise the main bulk of the fiber. It is well known that the ability of wool fibers to felt, tangle, and curl is dependent upon the direction and shape of the imbricated scale structure and that this cuticle serves to protect the fiber from chemical and mechanical degradation (figs. 1 and 8). It has been recently suggested by Mercer et al. [2, 3, 4], that these three dominant cellular structures are encased in an amorphous material that functions as a matrix and as an intercellular cement and that the cuticle layer may be covered by this same featureless keratinous material (figs. 1 to 6). These investigators and others have shown this amorphous plastic outer covering of the scales to be readily digested in an enzyme as is the featureless intercellular cement that exists between the scale and the cortex, as well as between and within the cortical cells themselves. The similar reaction to enzymic treatment suggests similar composition. Microscopy alone cannot disclose whether there

xists a continuous matrix of a single substance hat envelopes the differentiated cell structures or hether the keratinous material is made up of dif- erent protein molecules with varying properties.

The present study confirms, at least partially, he "matrix theory" of the morphology of the wool iber. Electron micrographs of the surface replicas f mechanically abraded and unabraded wool bers (shown in figs. 1, 2, and 3) reveal that the cale is heterogeneous in structure and consists, at east, of a double layer. The outer layer is a mooth covering for the under structure and shows o specific surface features (fig. 1). When this acquer-like coating is removed by mechanical brasion, a rigid striated structure is exposed fig. 2). These regular corrugations (ridges and urrows) run more or less parallel to the longitu- inal axis of the fiber. They are a feature of the cale itself and are not dependent upon, or a eflection of, the size and formation of the cortical ells. This is borne out by the fact that the ribbed tructure is seen in the overhanging portions of the cales under which there is no cortex (fig. 3). With reater degrees of abrasion, the scales are polished way leaving a smooth filamentary structure with light vestiges of the former imbricated surface fig. 4). Still more rubbing removes the next morphous layer under the scales and reveals the ortical cells themselves imbedded in the cemen- um (fig. 5). After such severe abrasion, the wool o longer manifests its characteristic filamentary tructure and, as such, is destroyed (fig. 6).

Thus far the present investigation indicates that he weaving process introduces very little change n the surface structure of the fibers. Some portions show degradation of the scale, but this is y no means typical. When compared with nwoven, undyed fibers, less than 10 percent of he fibers studied showed any modification (fig. 7). These alterations are very likely associated with he previous history of the fiber. It is not neces- arily a result of the weaving process. In the case of khaki-dyed woolens, similar evidence was noted (fig. 9). In a few samples where the fibers were ot washed in alcohol, some crystalline material as found imbedded in the replica. This may have een some of the dyestuff that had lodged on the outer scale surface. In the case of fibers that had been chlorinated in a 1-percent aqueous solution of calcium hypochlorite long enough to wet its entire length and rinsed in a large quantity of cold water (figs. 10, 11, and 12), the sacs and blisters formed (probably the Allwörden reaction) indicated a violent attack on the amorphous lacquer-like layer of the scales. The general erosion that took place exposed the characteristic striated substructure of the scale that withstood the action of chlorine. The exposed scale edges showed the greatest amount of attack (fig. 12). The treatment given the fibers was, of course, much more drastic than that used in some commercial processes for shrink-proofing woolens.

With the foregoing method, the structural changes in textile fabrics resulting from various physical and chemical factors can be studied. Alterations in the physical structure brought about by such means as abrasion, flexion, tension, acid, alkali, chlorine, heat, sunlight, and other elements of degradation make wear a complex phenomenon with a large variety of contributing factors. Before statistical correlation of any microscopic observations of laboratory wear versus actual wear may be obtained, a large number of tests interpreted against a broad background of performance in service is necessary. The "polishing" produced with Schiefer's uniform abrasion machine offers a systematic approach to a microscopic study of a worn fabric. The characteristics of fiber structure may in turn be correlated with the morphological modifications resulting from actual wear in service. Although the fundamental problem of the molecular structure of organic fibers cannot be solved by electron microscopy alone, considerable information may be determined that is of interest to the textile technologist and to those concerned with the subject of wear resistance.

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FIGURE 1.

Total magnification approx. × 2700

(electronic, × 716; optical, × 3.8).

Typical chromium-shadowed polystyrene negative replica of a wool fiber taken from unabraded, undyed, fine worsted fabric. The normal appearance shows the smooth lacquer-like coating on the imbricated cuticle. Faint striations may be seen that are part of the corrugated scale structure lying below this amorphous outerlayer.

FIGURE 2.

Total magnification approx. × 2800

(electronic, × 716; optical, × 4).

Chromium-shadowed polystyrene negative replica of a wool fiber taken from a mechanically abraded fine worsted fabric. The slight amount of abrasion removed the lacquer-like outerlayer of alternate areas. The middle area was protected from wear by the interlaced nature of the fabric.

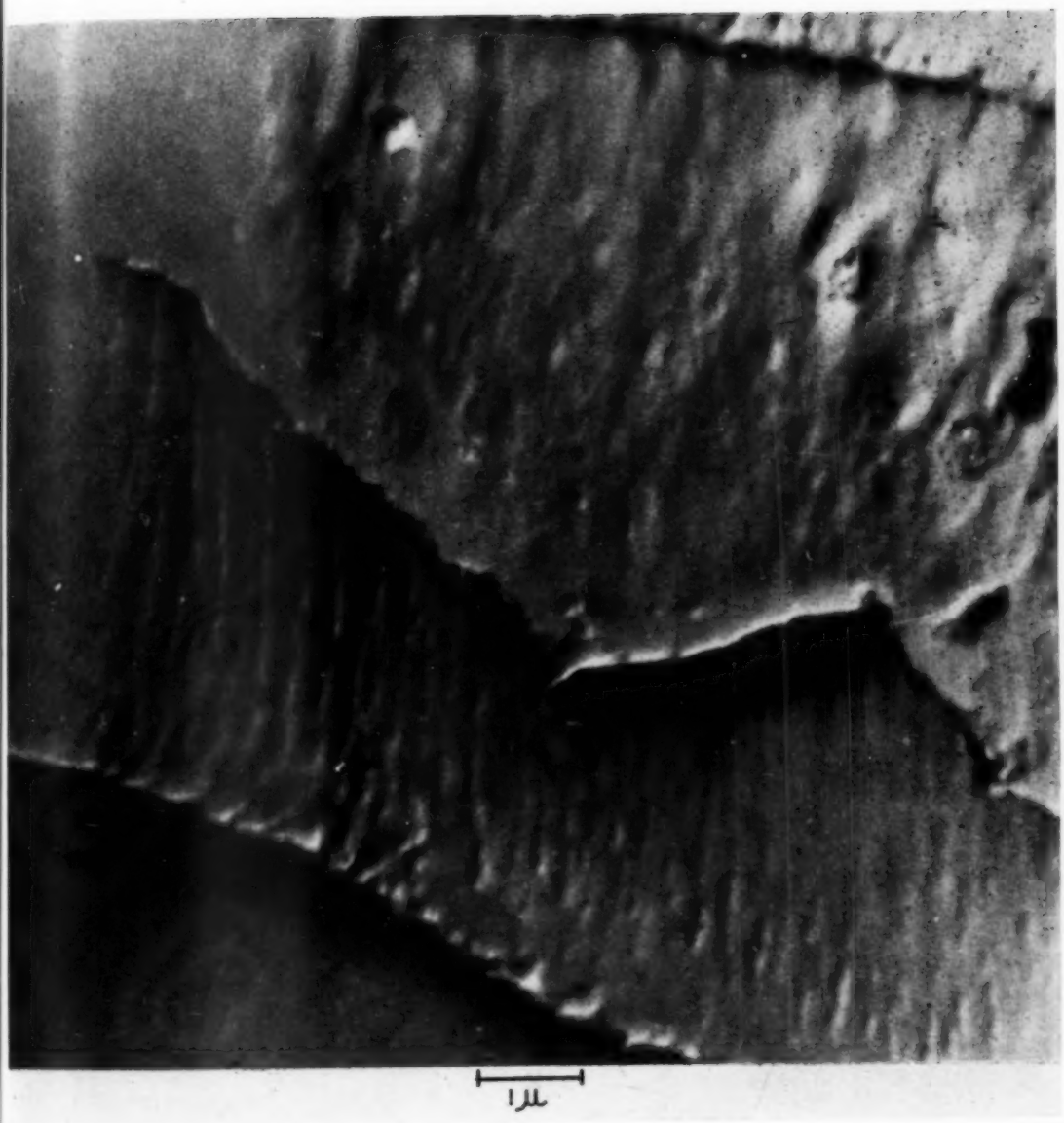

FIGURE 3.

Total magnification approx. × 16,500

(electronic, × 3600; optical, × 4.6).

An enlargement of the abraded area in the lower part of figure 2 showing the corrugated or ribbed underlying structure of the cuticle, in contrast with the smooth surface of the unabraded fiber (lower left). The longitudinal striations are an integral part of the scales themselves and not a reflection of the cortical cell formation underneath. Note the overhanging portion of a scale, in the upper left area of the replica, under which there is no cortex.

FIGURE 4.

Total magnification approx. × 2000

(electronic, × 716; optical, × 4).

Chromium-shadowed polystyrene negative replica of a wool fiber taken from the "debris" of mechanically abraded fine worsted fabric. Except for a few remnants, the scales have been removed and another comparatively smooth layer of material, the intercellular cement, lying between the cuticle and the cortex is exposed.

FIGURE 5.

Total magnification approx. × 2400

(electronic, × 716; optical, × 3.4).

Chromium-shadowed polystyrene negative replica of a wool fiber taken from the "debris" of mechanically abraded fine worsted fabric. Some scale remnants may be seen, but for the most part the coarse striated structure is that of the cortical cells beneath, indicating a greater degree of abrasion than that shown in figure 4.

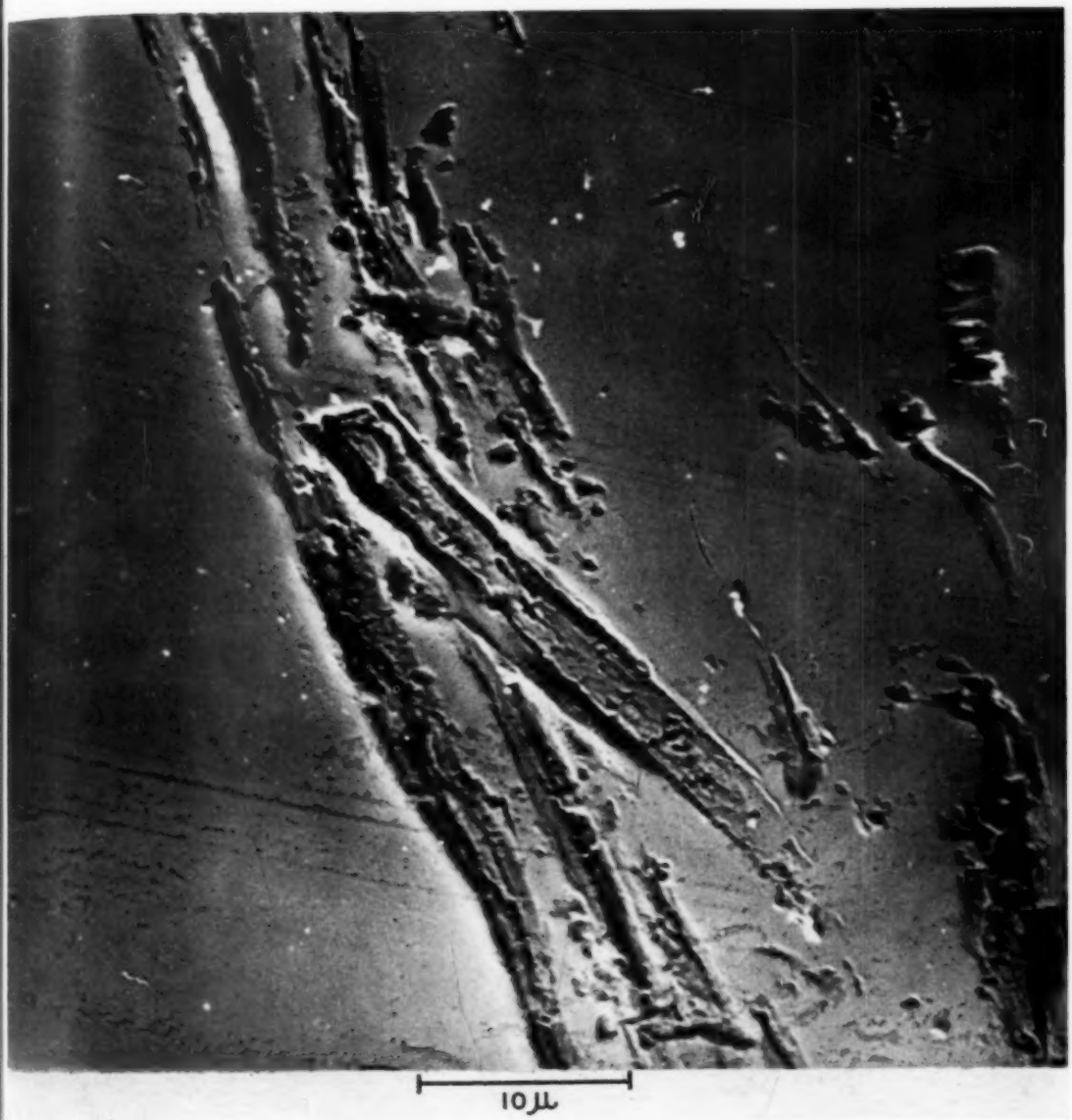


FIGURE 6.

Total magnification approx. × 3300

(electronic, × 716; optical, × 4.6).

Chromium-shadowed polystyrene negative replica of the remains of a wool fiber from severely mechanically abraded worsted fabric. The size of the structure lying across the center is about that of a cortical cell. Inasmuch as the soft cortex is easily deformed and the fiber is in the last stages of its filamentary formation, interpretation is questionable.

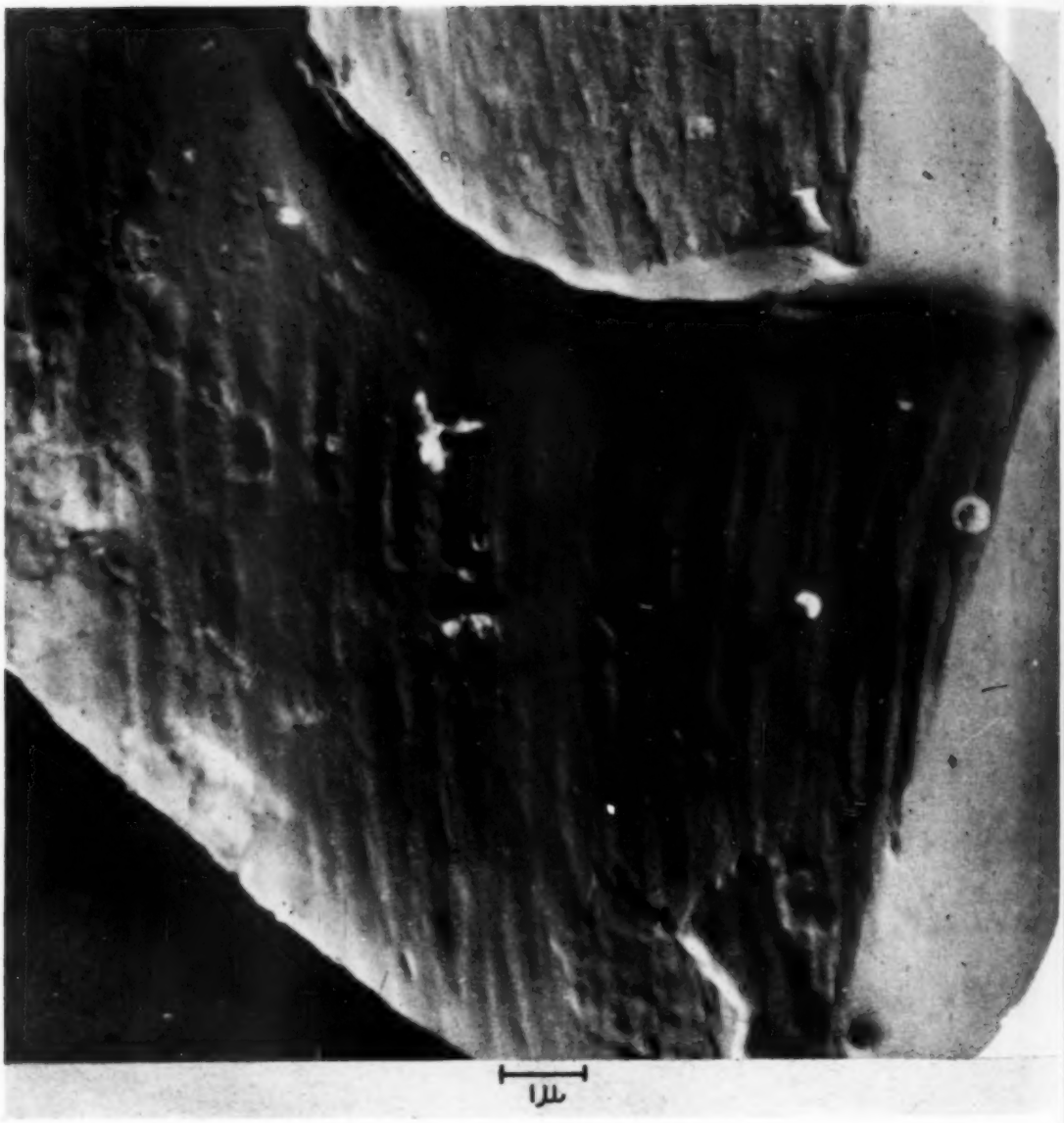


FIGURE 7.

Total magnification approx. × 13,300

(electronic, × 3600; optical, × 3.7).

Chromium-shadowed ethyl cellulose negative replica of an atypical fiber taken from unwashed, undyed, worsted yarn showing slight surface degradation associated with the previous history of the wool. Note the undegraded, smooth scale surface in the lower left corner. Here the thicker lacquer covers scale is more deeply imbedded in the thermoplastic film

FIGURE 8.

Total magnification approx. × 2000

(electronic, × 540; optical, × 4.8).

Chromium-shadowed ethyl cellulose negative replica of two fibers from an unwashed, undyed, worsted yarn showing the bulging distortion of one resulting from excessive contact pressure on the fiber. Note that the scale structure has stretched to more than double its surface area in order to accommodate the deformation without rupture. The smooth outerlayer is still intact, indicating its plastic nature.



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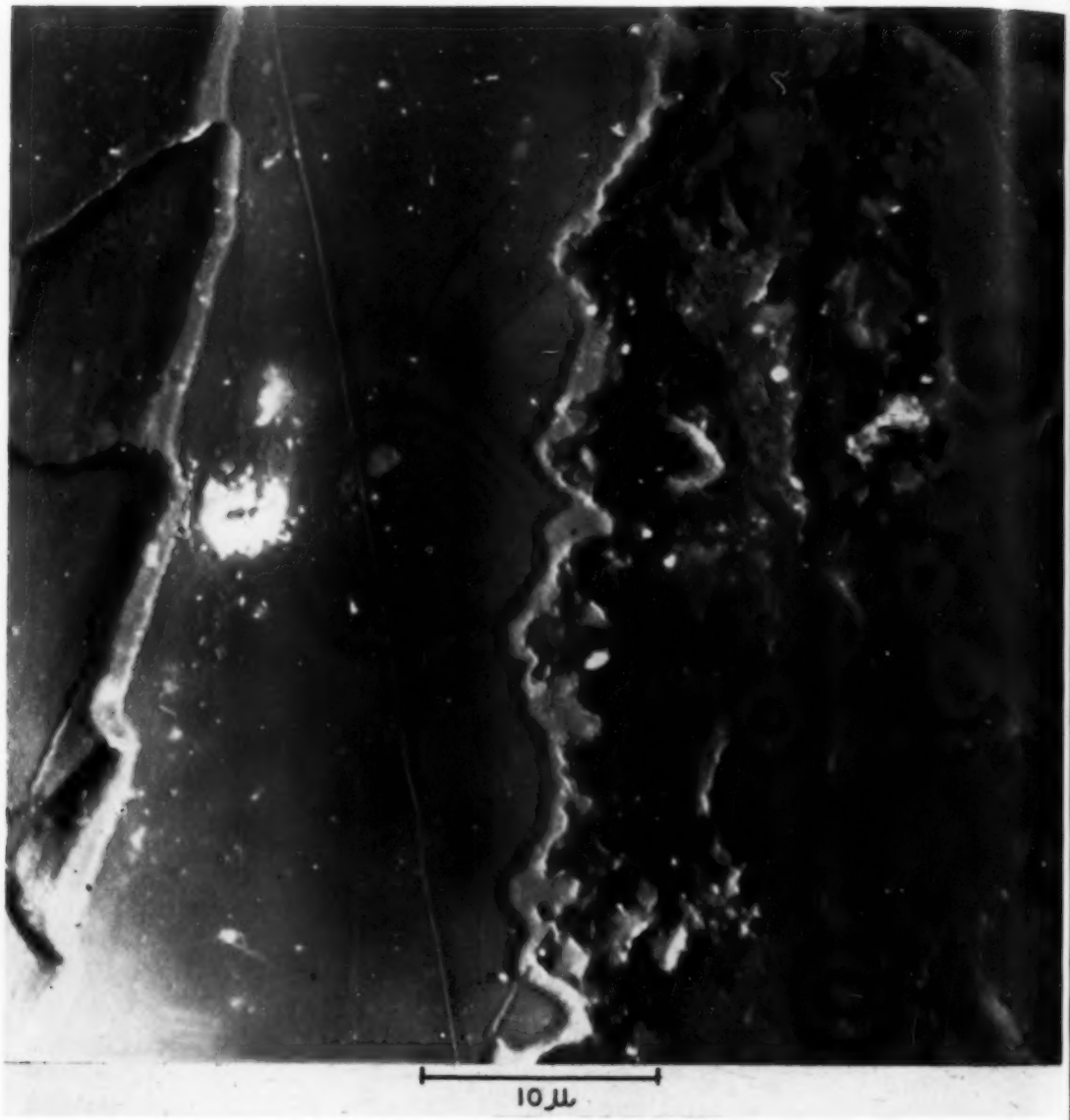


FIGURE 9.

Total magnification approx. × 3600

(electronic, × 716; optical, × 5).

Chromium-shadowed polystyrene negative replica of wool fibers taken from untreated khaki-dyed fabric. The normal surface structure of one fiber may be compared with the features of one damaged by an unknown agent, probably chemical.

FIGURE 10.

Total magnification approx. × 3600

(electronic, × 716; optical, × 5).

Chromium-shadowed polystyrene negative replica of a fiber taken from undyed worsted fabric, immersed in a 1-percent aqueous solution of calcium hypochlorite long enough to wet it, and then rinsed in cold water. The fiber still exhibits its filamentous structure.

FIGURE 11.

Total magnification approx. × 17,000

(electronic, × 3600; optical, × 4.7).

An enlargement of the area in the lower part of figure 10. The erosion of the superficial lacquer-like coating exposed the characteristic striated substructure of the scales that was more resistant to the chemical attack.

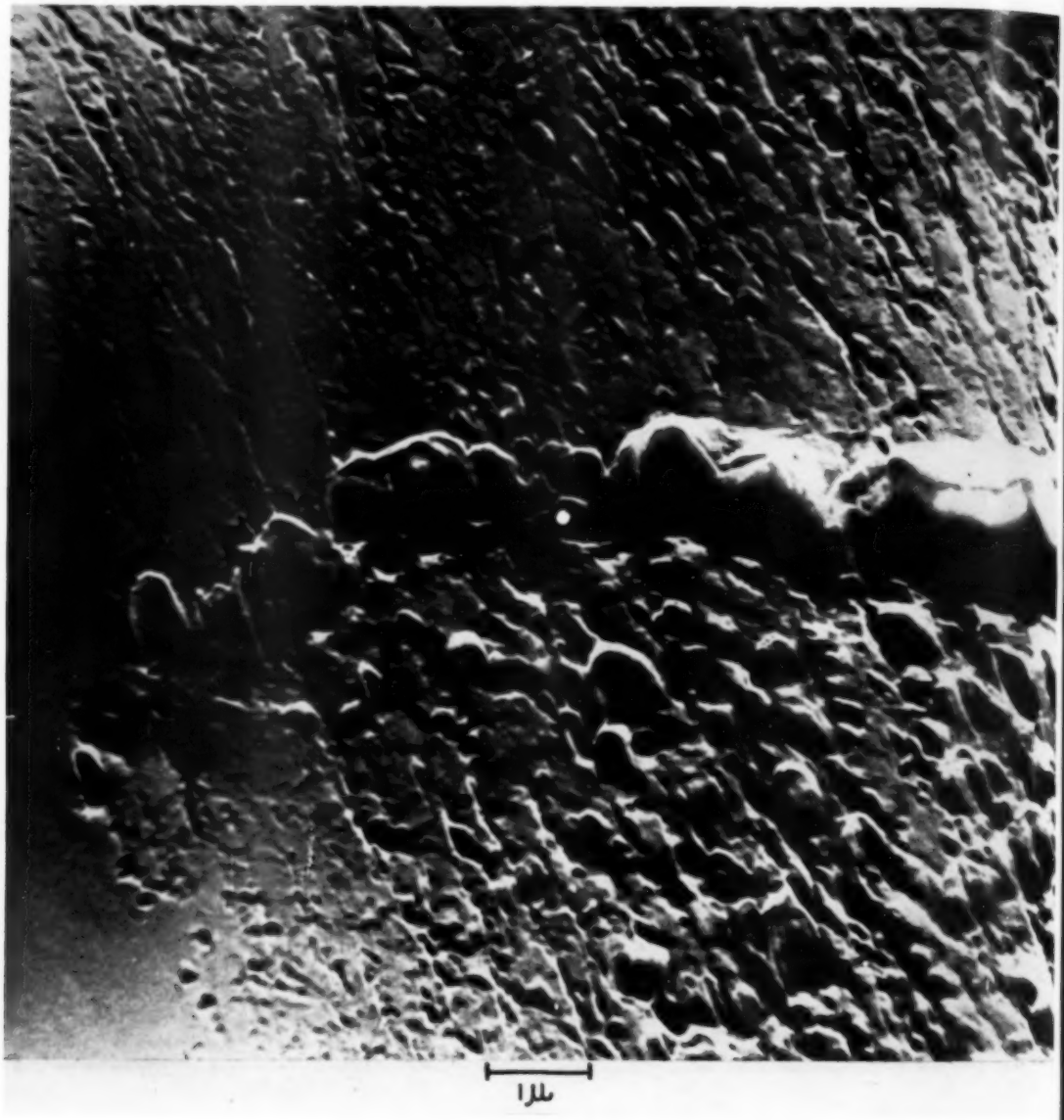


FIGURE 12.

Total magnification approx. × 16,500

(electronic, × 3600; optical, × 4.6).

Chromium-shadowed polystyrene negative replica of a wool fiber after chlorination, showing what is probably the blistery sacs of the Allwörden reaction on the lacquer-like scale surface with evidence of concentrated attack at the edges of the scale.

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